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B-465

GEORGIA INSTITUTE OF TECHNOLOGY
Solid State Sciences Division
Engineering Experiment Station
Atlanta, Georgia 30332

SEMI-ANNUAL STATUS REPORT
Project No. B-465

CARBON DISTRIBUTION PROFILES IN LUNAR FINES

by

Raymond K. Hart

Research Grant NSG-9040
1 February 1976 to 31 January 1977

Performed for

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ABSTRACT

The purpose of this work is to investigate radial distribution profiles of elemental carbon in lunar soils consisting of particles in the size range of 50 to 150 μm .

This report is concerned with the initial experiments on specimen preparation and the analysis of prepared specimens by Auger electron spectrometry (AES) and scanning electron microscopy (SEM).

Results from splits of samples 61501,84 and 64421,11, which were mounted various ways in several specimen holders, are given in this report. A low carbon content has been observed in AES spectra from soil particles that had been subjected to sputter-ion cleaning with 960eV argon ions for periods of time up to a total exposure for one hour. This ion charge is sufficient to remove approximately 70 nm of material from the surface. All of the physically adsorbed carbon (as well as water vapor, etc.) would normally be removed in the first few minutes, leaving only carbon in the specimen, and metal support structure, to be detected thereafter.

A number of problem areas have been identified and consideration is given to methods which may be employed to overcome these difficulties.

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I INTRODUCTION

This report describes the progress made in developing a practical method for the determination of both spatial and depth distributions of carbon in lunar fines.

The lunar soils that were collected at the Descartes site during the Apollo 16 mission have been analyzed for their total carbon content⁽¹⁾, and these analyses show the carbon content to lie approximately within the range 60-250 ppm. Comparing these data with carbon data from soils obtained during previous missions, show that the carbon content of most lunar soils is similar⁽²⁾. The origin of carbon found in the lunar regolith is believed to be the solar wind.

The composition of Apollo 16 soils, of which carbon is a very minor constituent, is largely made up of the following materials, SiO_2 (45%), Al_2O_3 (27%), CaO (16%), MgO (6%), and FeO (5%): the numbers in parentheses are averages which were derived from the analyses of all Apollo 16 soils⁽³⁾.

Samples of Apollo 16 soil requested for this investigation were selected on the basis of their overall carbon content and particle size. Four samples were received on April 9, 1976, whose total carbon contents ranged from 65 $\mu\text{g/g}$ to 280 $\mu\text{g/g}$: the sample numbers and sampling locations at the Descartes site are shown in Fig. 1. For optimum utilization of grid openings in the specimen holders we proposed for this research, discrete particles in the size range 50 to 150 μm are necessary. This size range corresponds closely to the 63-125 μm sieved size fraction used in particle size analyses of lunar fines.

In order to equate the carbon content in our samples to either surface or indigenous carbon, a method consisting of argon-ion beam profiling in conjunction

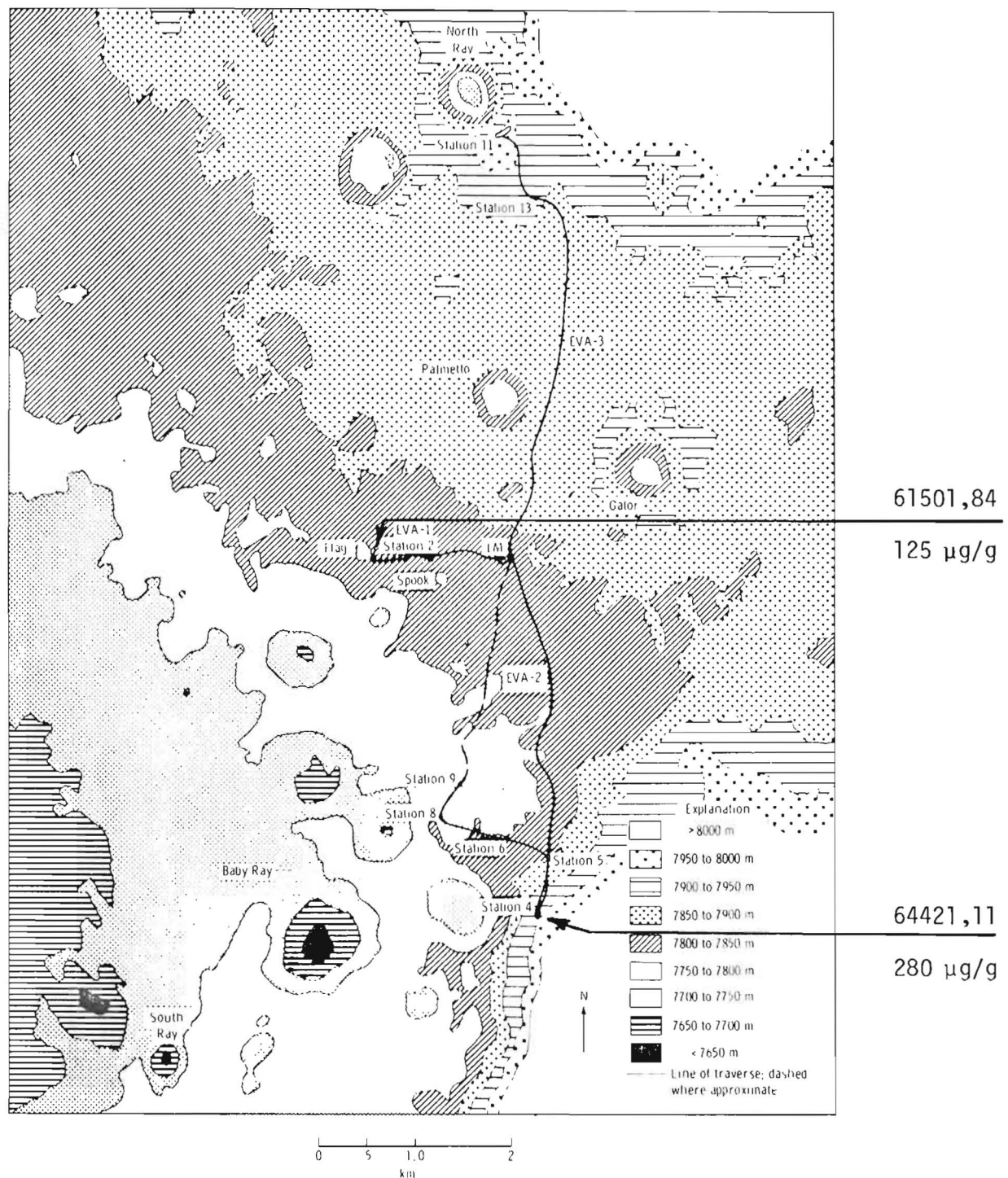


Fig. 1. Hypsographic map of Descartes site showing Lunar Module and sites visited during the Apollo 16 mission (NASA SP-315, p.6-63, 1972). Samples that have been analyzed during this study are listed as well as their reported total carbon content (Ref. 1).

with scanning Auger-electron spectrometric microscopy is being employed⁽⁴⁾,

Auger-electron spectroscopy (AES) is particularly sensitive to the lower atomic number (Z) elements, such as beryllium, boron and carbon. In carrying out AES analyses carbon is almost invariably an obnoxious impurity as well as being the main constituent of surface contamination⁽⁵⁾. Under the environmental conditions used to carry out AES analyses, carbon and other surface contaminants can be readily removed before, as well as during, analysis by bombarding the surface area being analyzed with a beam of ionized argon. However, by so doing, this analytical method can no longer be strictly called non-destructive, since both the sample's mass and surface topography are changed. Also, it must be remembered that material can be removed by, or diffuse from, the primary irradiated zone by reacting with the electron beam⁽⁶⁾. Consequently, it is extremely important to keep the electron dosage as small as is practical during the analysis.

Also, quantitative analysis of a profiled surface must take into consideration changes in the surface topography due to selective removal of material while under ion-beam irradiation. Topographical features are most successfully monitored by scanning electron microscopy.

II EXPERIMENTAL

A. Material

Four samples of Apollo 16 soil, each having a mass of approximately 0.1g, were received on April 8, 1976. The sample numbers were: 61501,84; 64421,11; 65701,68; 67701,9. Up to the time of writing this report only the sample containers holding samples 61501,84 and 64421,11 have been opened. These two samples were observed to be light grey powders. During subsequent handling of some of the particles with "demagnetized" stainless steel tweezers, they appeared to be slightly magnetic.

Scanning electron micrographs taken of very small portions of these powders during the course of this investigation showed the grain size in these two samples to vary from about 3 μm to over 300 μm . Furthermore, most of the particles in the size range of interest (50-150 μm) were observed to be agglutinates of varying sized particles, as shown in Figs. 2 and 3, and not discrete particles. This feature has proved to be particularly troublesome and has resulted in technique changes and some undesirable results. We will return to this question of particle morphology at various places throughout this report.

B. Specimen Preparation.

1. Environmental Chamber. The original intention for preparing samples for AES analysis, as described in our proposal, was to carry out all the specimen preparation in a stainless steel environmental chamber under a slight positive pressure of dry nitrogen. Because of the nature of the sample material, it was found to be unpractical to handle the material via the rubber gloves protruding through the chamber wall.

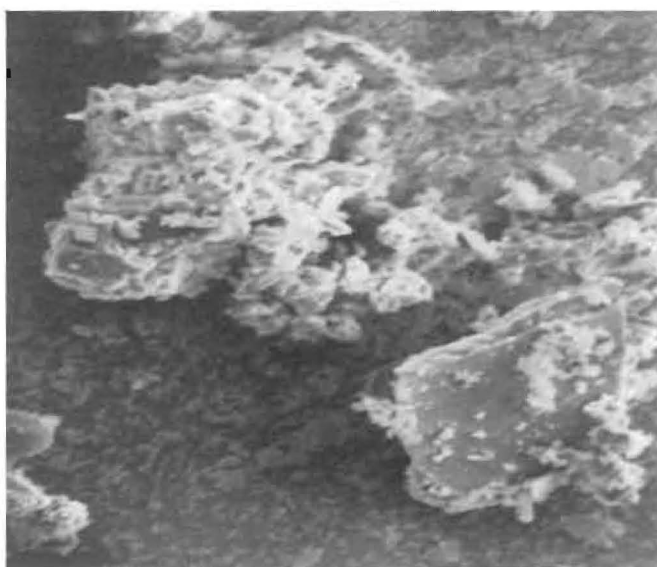
As a solution to this problem, samples to date have been loaded into



[.1mm]

x120

Fig. 2. SEM of sample 64421,11a attached to copper platen with conductive silver paint.



[.1mm]

x120

Fig. 3. SEM of another area of mounted specimen used in Fig.17. Note range of particle sizes from several microns to over 300 microns,

holders within the environmental chamber under atmospheric conditions with the front glass cover partly opened and the whole of the preparation area illuminated with moderately intense ultraviolet radiation. This technique has been shown to prevent carbon buildup on clean surfaces⁽⁷⁾, and should prevent all but the very minimum buildup of carbon on our samples before they are subjected to AES analysis - this carbon is customarily removed during the first ion cleaning step.

The transfer of soil to the grids, and the grids to the holder were carried out under a variable magnification stereo microscope. All the specimen handling equipment, including the specimen support screens and holders, were thoroughly cleaned before use in the environmental chamber or for transport of specimens to the spectrometer, etc.

This cleaning process consists of the following steps:

- 1) Vapor degrease components in trichloroethylene.
- 2) Ultrasonically clean in an aqueous solution containing 50 ml of MICRON[®] per liter.
- 3) Wash in distilled water and rinse in a stream of methanol (ACS grade).
- 4) Immerse in a hydrogen peroxide (30 percent) solution containing 10 percent ammonium hydroxide, effervescing at 80°C. Remove after the liquid is spent.
- 5) Rinse in a stream of methanol and dry in a stream of pure nitrogen.
- 6) Transfer items to the environmental chamber.

Items that have been cleaned by this procedure have been found to be free from carbon as a surface contaminant.

2. Specimen Grids and Holders. A specimen holder was designed so as to

make use of the quick charge, plug in, feature of our electron spectrometer. One of the two units is shown in Fig. 4. The base is a commercially manufactured type HC-6 base of a quartz resonator container and mates with a two pin ceramic bodied socket, which is mounted on the specimen manipulator in the AES.

The round specimen holder section holder section is attached to a molybdenum support bracket with a 2-56 stainless steel screw. In turn, the specimen grid is secured against a flange at the bottom of the opening by a copper collar which bears against the molybdenum support bracket. The round section is made from very high purity copper and is heavily gold plated.

A 200 mesh hinged gold grid (see Fig. 5) was selected at the beginning of this project to mount the lunar soil samples. On shaking a small amount of sample 61501,84 onto such a grid, it was quickly discovered that essentially all the soil particles fell through the 90 μm openings. Then, all except one on two particles that remained on the grid broke up and passed through the grid when it was folded and secured in place by the retaining ring.

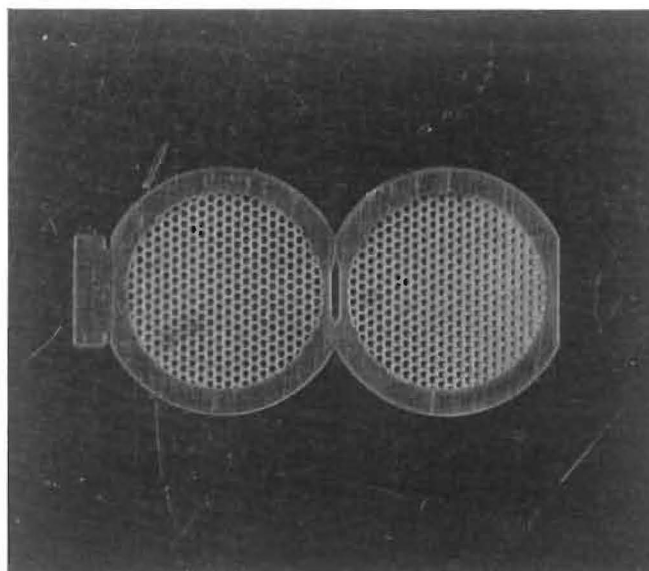
Some 400 mesh (40 μm openings) copper grids were on hand so an attempt was made to use this type of grid. A few more particles were retained between these grids, but they presented another problem - a greatly reduced free area. Also, it was observed that the captured particles were not securely held in the grid sandwich because of the grid's flexibility. Some results were obtained from soil supported between 400 mesh grids.

Another approach was used in preparing the last sample that we have analyzed. The technique was to replace the rear grid with a solid copper platen (25 μm thick) and to attach soil particles to it with a very thin layer of silver conducting paint. This paint is composed of pure silver particles suspended in



x4

Fig. 4. View looking in the primary beam direction of a specimen holder used to mount lunar fines for AES/SEM.



x11

Fig. 5. View of a 200 mesh hinged gold specimen mount.

ethanol. A 300 mesh hexagonal copper grid (50 μm openings) was used to complete the specimen mount.

C. Analysis

Electron spectrometric analyses were carried out in the scanning Auger electron spectrometer shown in Fig. 6. The system uses a cylindrical mirror analyzer (J) with a 1 percent energy resolution, a 0-5 keV primary electron gun (D) and a 0-1 keV Argon ion gun (L). Three electrostatic lenses in the electron gun focus the beam to about an 8 μm diameter spot in the specimens plane (M). Deflection coils (E) allow the beam to be scanned on the specimen surface in a variety of ways, e.g., raster, line scan, point-to-point. A minimum image magnification of 28 can be obtained in the meter mode. The ion beam can be focused to about a 4mm spot on the specimen, which is rotated about 90° to receive the ion beam.

Auger-electron data were obtained with the spectrometer system operating at a base pressure of $1.2 \times 10^{-7} \text{ N/m}^2$ (9×10^{-10} torr). During the majority of runs, an electron beam energy of 3900eV was used, although experimental runs were made with the beam energy as low as 1200eV. In all instances, the beam current at the specimen was about $2 \times 10^{-8} \text{ A}$.

In order to reduce charging and also to prevent radiation induced changes to the specimens, the primary beam was always scanning the specimen. AES data were usually collected with the electron beam scanning the desired area of the specimens surface at a rate of one frame per 8 seconds. At a magnification setting of 1.52 (x306), a rectangular specimen area 400 μm long by 300 μm wide was illuminated. This area encloses about 9 openings in a 300 mesh grid.

Argon ion cleaning and profiling was carried out at an argon pressure of $7.7 \times 10^{-3} \text{ N/m}^2$ (5.8×10^{-5} torr). The ion gun was operated in the focused condition

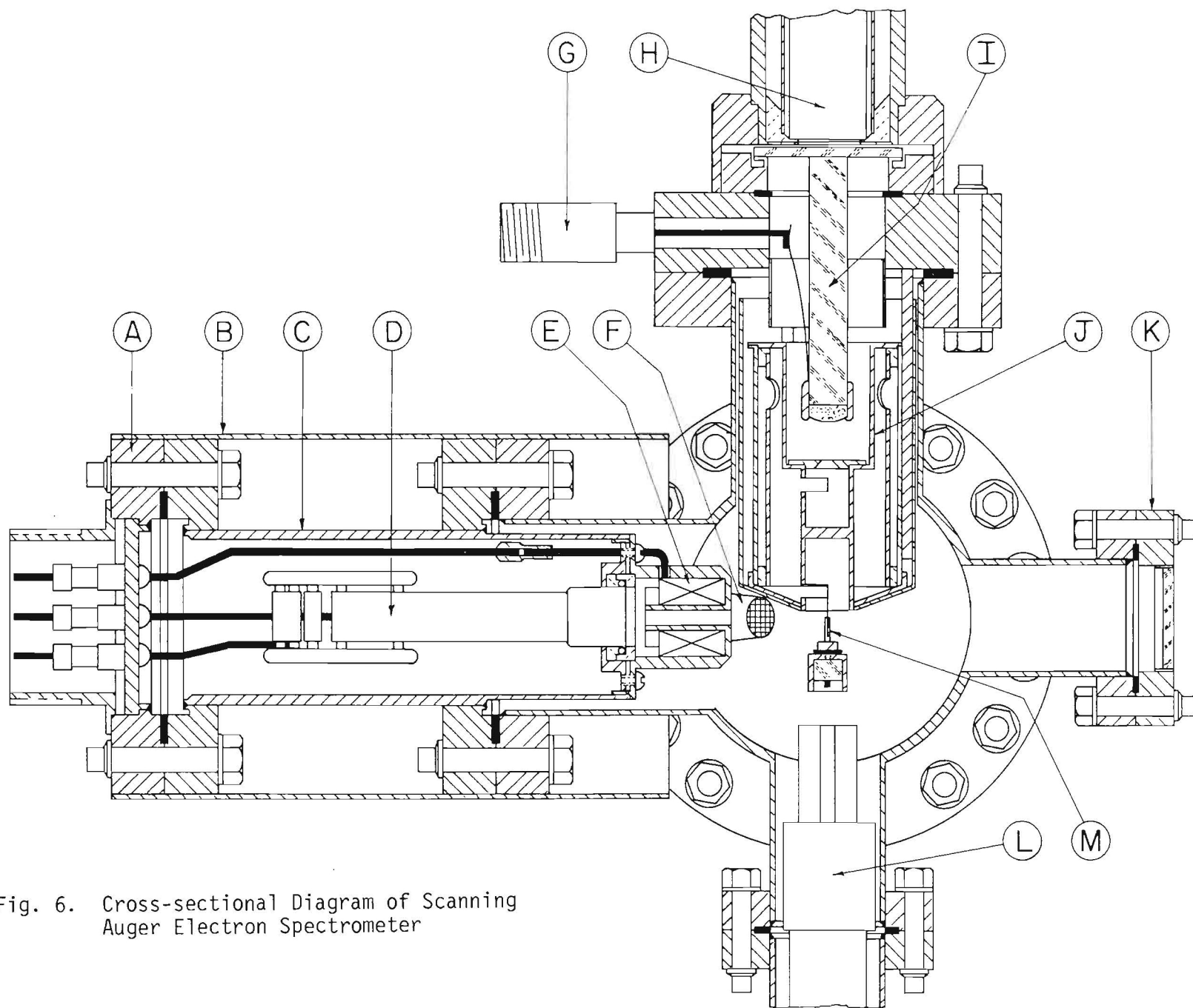


Fig. 6. Cross-sectional Diagram of Scanning Auger Electron Spectrometer

at 960eV and 8×10^{-6} A.

Each ion bombardment was for a period of 15 minutes, which corresponds to the removal of approximately 45nm (rate of 3nm/min). This sputtering rate was determined from earlier work on quartz surfaces. Also, in the case of quartz, carbon and water surface contaminants were completely removed during the first 4 minutes of ion bombardment.

Low resolution absorbed current images were recorded of the areas used to obtain AES data. These images were used to reidentify the analyzed regions of each sample when the samples were examined in a regular SEM. The complete holder was mounted in the SEM so as to avoid disrupting the particles in the specimen from their original positions.

III RESULTS

A. Sample 61501,84

Three specimens have been prepared from this sample. From the first split, 84a, two specimens were prepared, the first with the soil particles between 200 mesh gold grids, and the second with the soil particles between 400 mesh copper grids. The second split, 84b, was used between two 300 mesh hexagonal copper grids.

Although the specimen using 200 mesh grids was subjected to AES examination, no useful data were obtained. This situation was due to the non retention of the soil particles by the grids.

When a switch to 400 mesh grids was made, a sufficient number of soil particles were retained in the grid sandwich to show up in the electron images, see Fig. 7, which were recorded in the AES. Several of the larger particles were selected for AES analysis.

Before the lunar soil was placed between the two 400 mesh grids used to prepare specimen 61501,84a, the grids were mounted in the specimen holder and analyzed in the AES. An initially strong carbon peak was essentially removed from the spectrum by sputter-ion cleaning for 15 minutes, as is shown in Fig. 8. This procedure was also carried out in all successive runs to obtain a data base from the specimen supports. With soil particles in position a prominent carbon peak was again a prominent component of the AES spectrum. However, after sputter-ion cleaning for 15 minutes, the carbon peak was substantially reduced and many other spectral lines appeared, as shown in Fig. 9. The elemental contributions from the soil particles are calcium, carbon, iron,

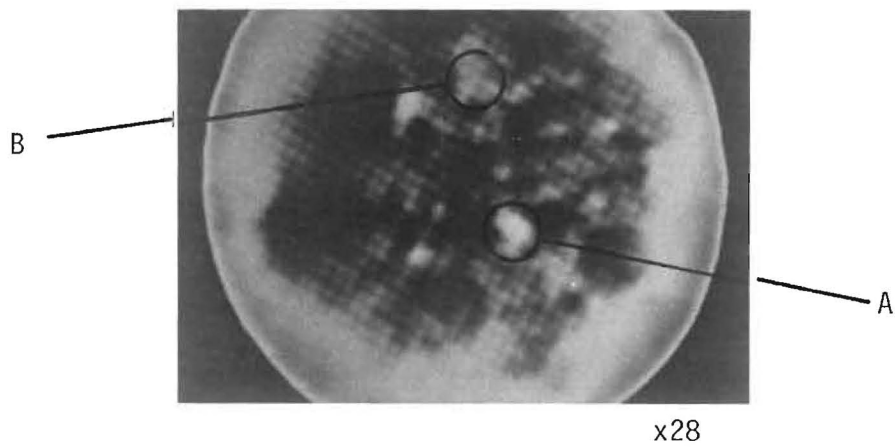


Fig. 7. Image of sample 61501,84a in the AES before analysis. Areas marked by A and B were selected for AES.

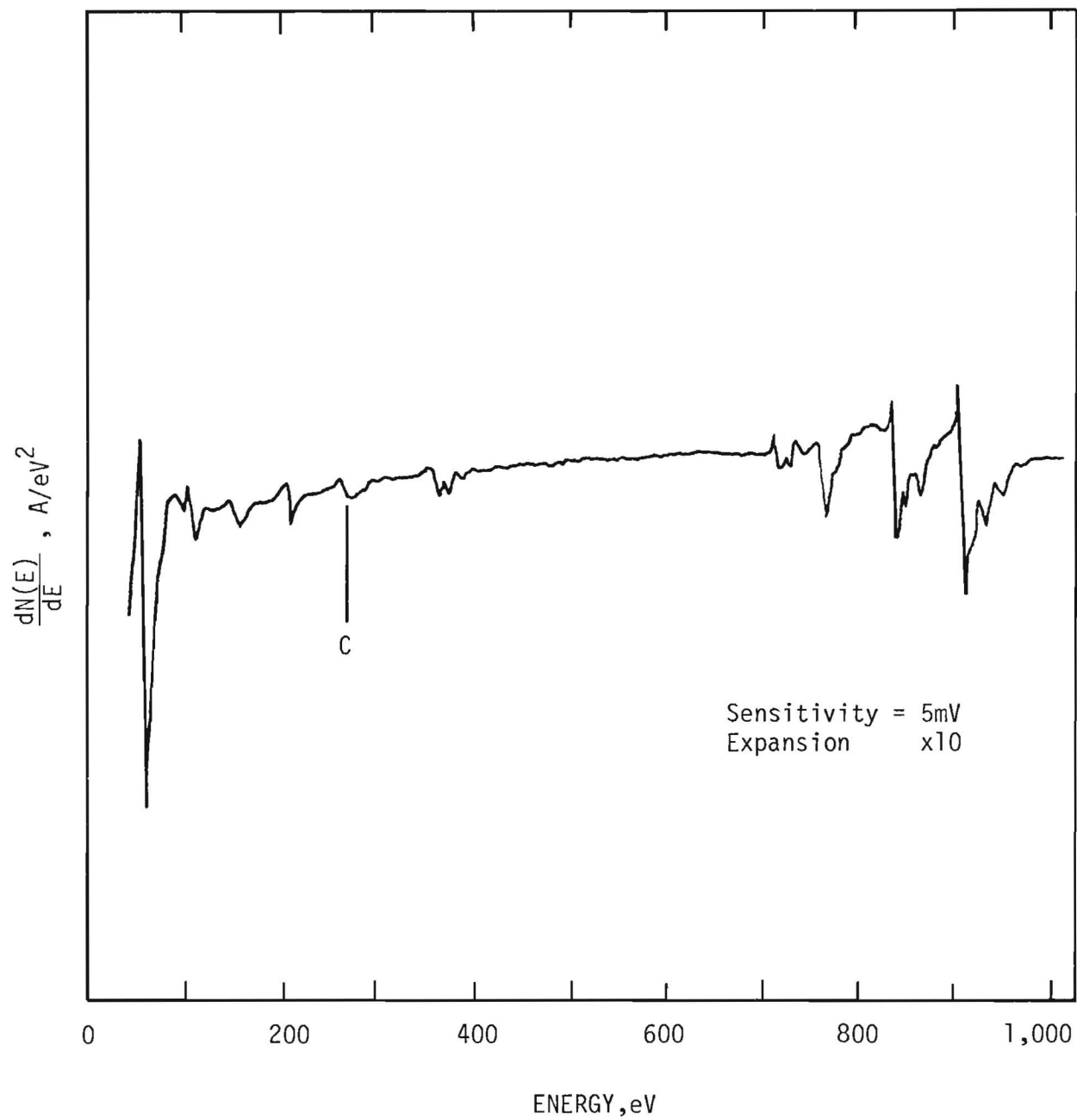


Fig. 8. AES from a 400 mesh copper grid in gold plated copper holder #2. Exposed surface was ion cleaned for 15 minutes.

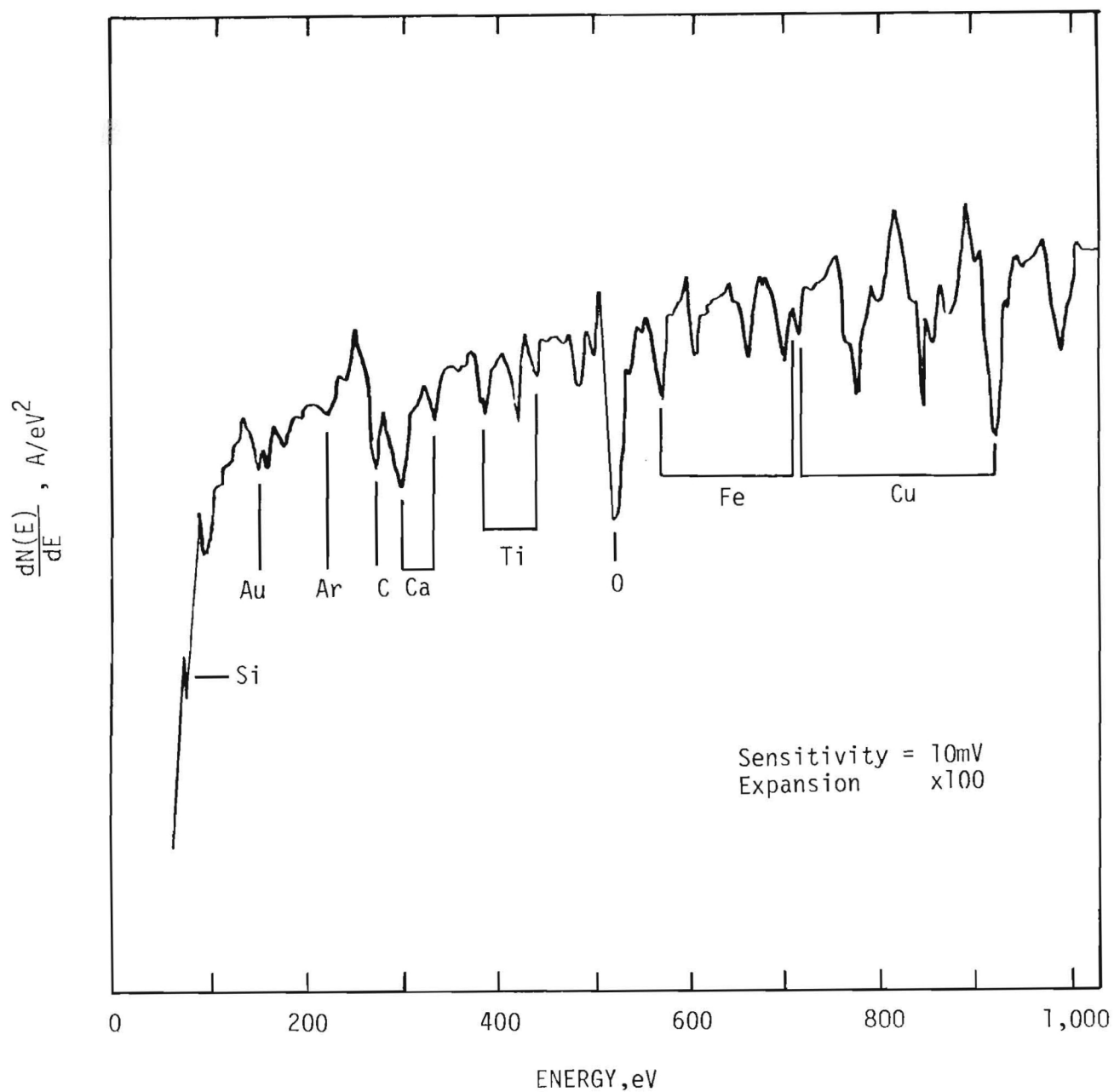


Fig. 9. Sample 61501,84a contained between two 400 mesh copper grids. AES recorded after 15 minutes of sputter-ion cleaning.

oxygen, silicon and titanium. The copper is from the support grids and the gold from the holder - sputtered onto the sample area.

After several more 15 minute ion bombardment periods, the spectrum in Fig. 10 was obtained. At this point of time, most of the elemental contributions from the soil had disappeared, with the exception of carbon, iron and oxygen.

Observation of the exposed specimen surface by SEM after a total of 60 minutes of ion bombardment showed the remaining particles to be generally smaller than the grid holes and scattered around the central region of the grid - see Figs. 11 and 12. None of the samples were metallized before SEM examination, so a certain amount of charge buildup was experienced. This effect is seen as horizontal streaking in the electron micrographs. Although the charging effect detracts from the quality of the image, it is easy to see under moderate magnification conditions (see Fig. 13) that the larger particles are agglutinates and not solid chunks. From the observed change in the AES data between 15 and 45 minutes, it is reasonable certain that the ion bombardment contributed to a breakdown and scattering (with considerable loss of material) of particles over the outer grid surface.

The AES data we obtained from the 84b split were essentially the same as those data given for the 84a split and will not be repeated herein.

B. Sample 64421,11a

Only one specimen has been prepared from this soil sample to date. The method of specimen preparation using a solid platen and silver paint appears to have considerable possibilities in this type of investigation. As Fig. 14 shows, a few large particles were securely anchored into place, but their

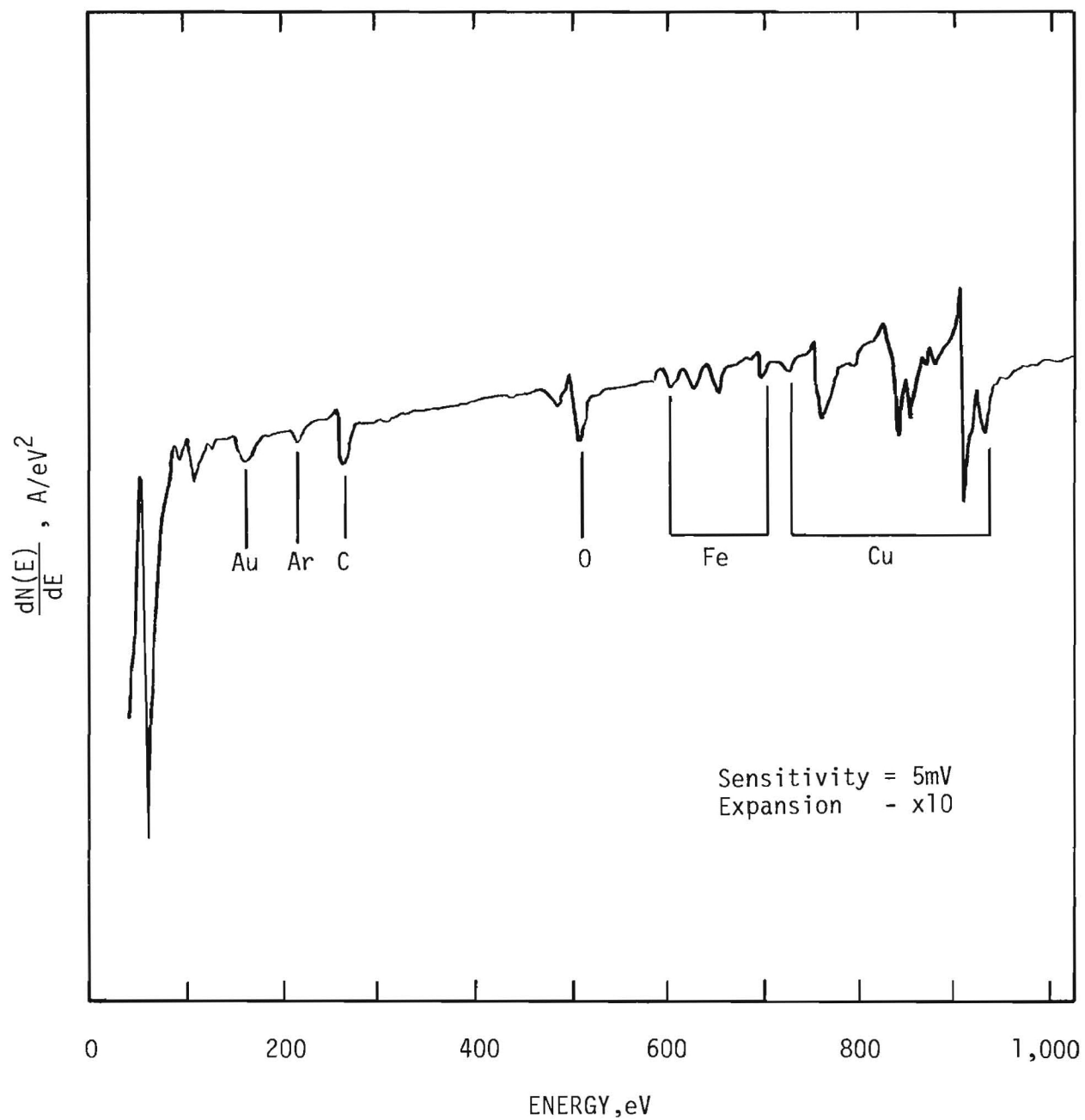
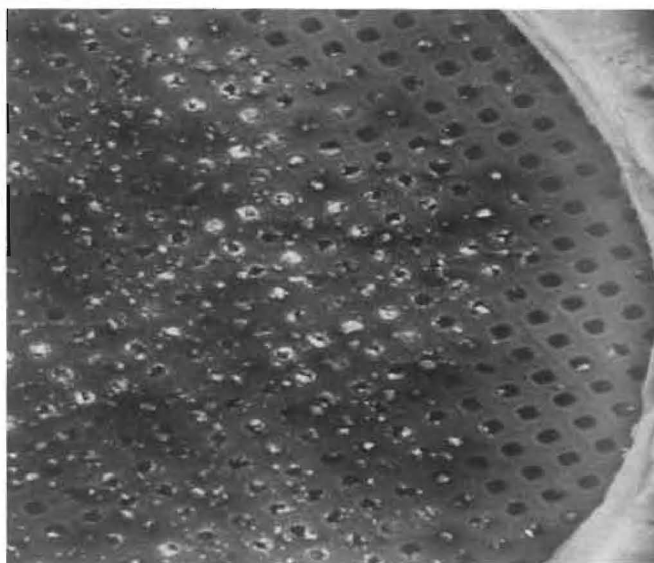
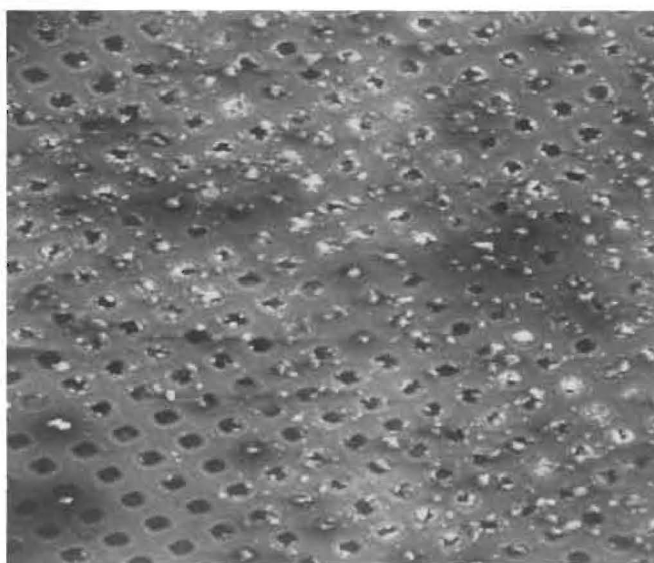


Fig. 10. AES from area B (see Fig. 7) of sample 61501,84a after 45 minutes of sputter-ion cleaning.



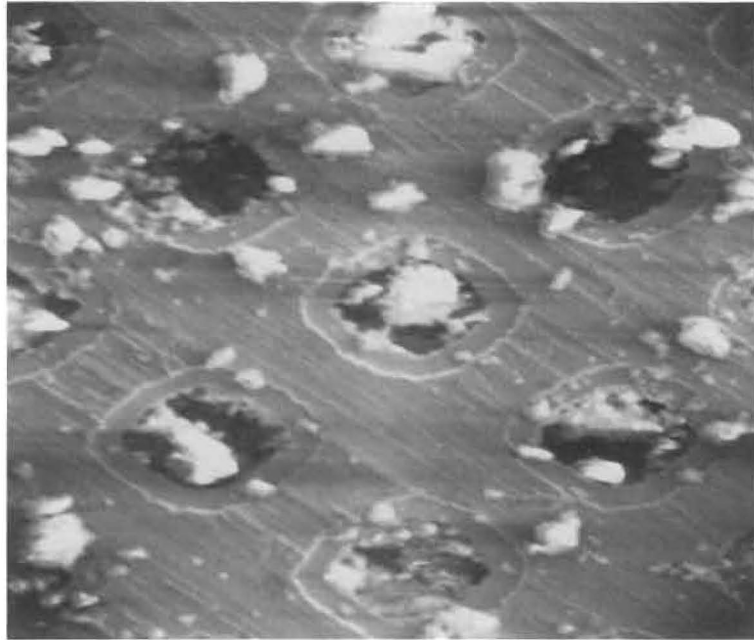
x60

Fig. 11. Section of 400 mesh grid containing particles of sample 61501,84a after AES analysis. Area A in Fig. 7 is located near top center in this view.



x60

Fig. 12. SEM from near center of same grid as shown in Fig. 11. Area B in Fig. 7 is located near left center of this image.



x350

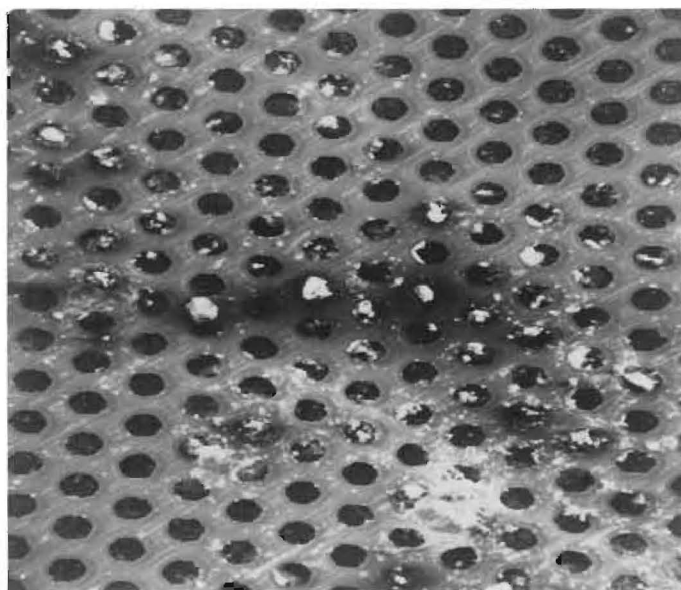
Fig. 13. Higher magnification SEM of part of the image shown in Fig. 12. Note the wide variation in particle size.

exposed areas were rather minimal. The use of grids with larger openings, e.g., 200 mesh or even 100 mesh, is indicated. However, if too large a grid structure is used, one runs the risk of electric charge buildup on the particle surface.

The degeneration of the ion bombarded particle surface into much smaller particulate matter is again evident in Fig. 14.

The AES shown in Fig. 15 was recorded from an as-prepared specimen of sample 64421,11a, with an ion cleaned 300 mesh copper support grid. Although the carbon peak is substantial, there was not sufficient carbon on the irradiated specimen surface to completely absorb all the Auger electrons from both the particulate matter and the front surface copper grid. Note that the response from silver is weak. With suitable screening, it should be possible to exclude the contribution of silver, and any associated carbon in the silver paint, from the primary spectrum.

After a total sputter-ion cleaning period of one hour, the copper response is dominant, see Fig. 16, but the carbon spectral line is still present, although it is reduced in height by a factor of 6 from the initial scan (Fig. 15). If future experiments can positively associate this carbon with particles, then we can begin to relate these carbon data to distribution profiles within the particle.



x78

Fig. 14. SEM from near center of sample 64421,11a. Soil particles were attached to solid copper platen with silver conducting paint and covered with a 300 mesh copper grid. Sample was sputter-ion cleaned for 60 minutes. AES data were recorded from the protruding particle at lower left center.

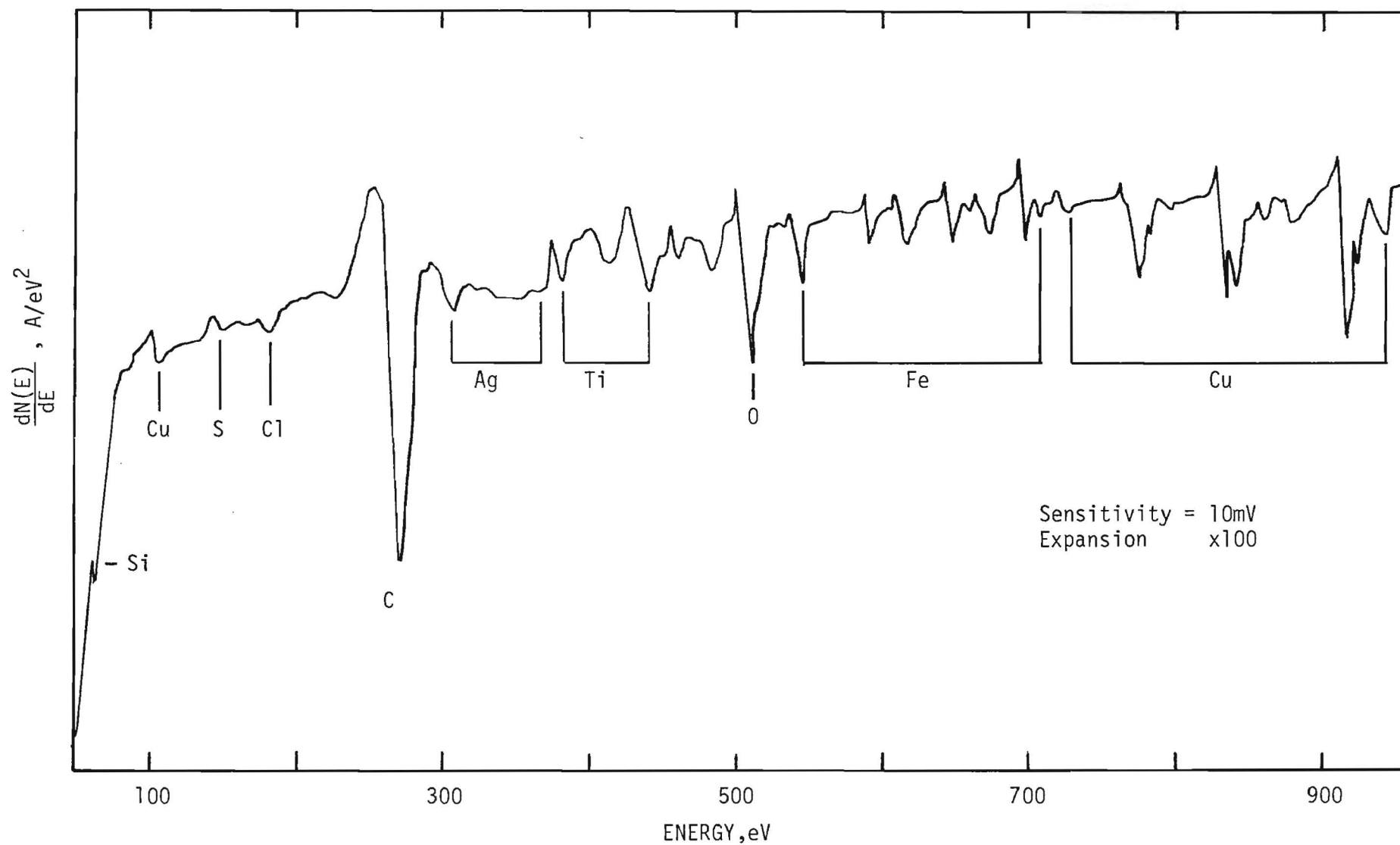


Fig. 15. Sample 64421,11a as shown in Fig. 14. This plot was recorded before the sample was subjected to any sputter-ion cleaning.

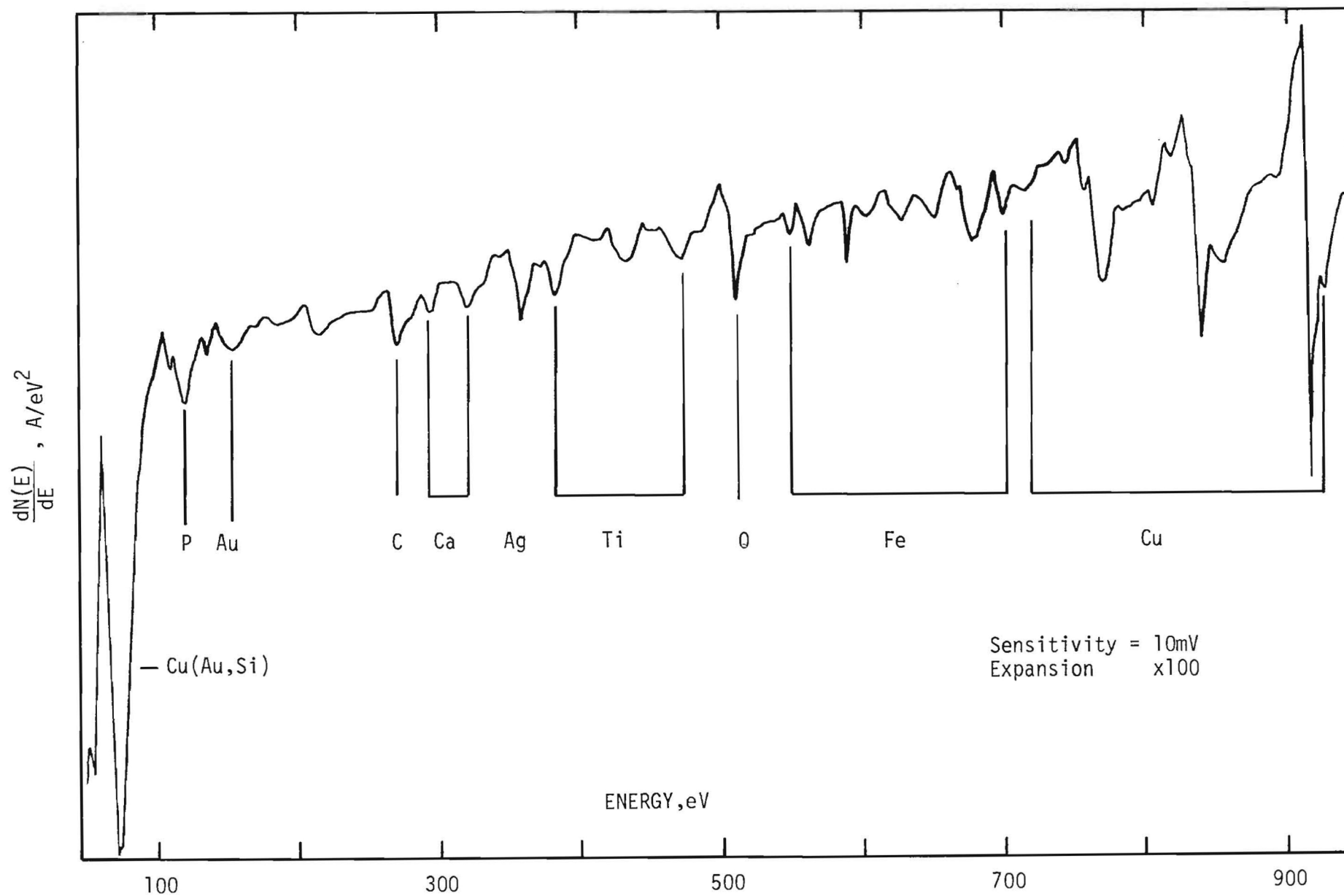


Fig. 16. AES from sample 64421,11a after the fourth successive 15 minute sputter-ion clean.

IV DISCUSSION

From the time of the first viewing of these lunar soil samplings, it was obvious that an innovative method would have to be devised to handle the specimen preparation. The initial concept of sandwiching discrete particles between microscope support grids with appropriately sized grid openings has previously been found to work well in both AES and SEM examinations.

In the present application of this technique only a very few physically homogeneous particles of suitable size were encountered in the samplings. The larger particles in the mounted specimens that have been mounted to date were mainly agglutinates which readily broke down into much smaller particles during mounting and/or during sputter-ion cleaning.

It should be possible to obtain a sufficient number of particles of the type shown in Fig. 3 to make up a specimen by sieving the soil samples through a grid and then selectively remove a suitable number of particles from the retained screenings. The present results indicate that it will still be necessary to adhere these particles to a platen with silver paint. There is still the possibility that these particles will break up during ion bombardment, and should this occur, it will have to be concluded that it will not be feasible to analyze these samples by depth profiling in the AES. Should this situation develop, then either a different type of sample will be necessary, or else the whole procedure dropped as being unsuitable for investigating this particular type of material.

The presented AES data show that material (gold in the present case) which has been removed by ion bombardment can easily deposit on the cleaned surface.

Naturally, the deposited material will exclude Auger-electron data from the derived spectra. Preventing this deposition process from occurring is difficult to accomplish, especially when the target area consists of both metals and insulators.

Sometimes it is possible to change the redeposition rate of the sputtered materials by changing the incident angle of the ion beam. However, if this angle is greatly increased from the surface normal, anisotropy is more likely to occur in the sputtering process and with our type of specimen shadowing may be an important factor. Neither of these effects are as important as the prevention of the material deposition during sputter-ion cleaning. No quick solution in this problem area is foreseen.

Another difficulty in quantifying the carbon response in the current spectral data is the partial overlapping of the carbon and calcium responses in the energy range between 260 and 300eV. This feature is noticeable in Figs. 9 and 16 with the carbon line (272eV) and the calcium doublet (291 and 294eV). A higher resolution spectrometer than the one used in this work, which has an energy resolution of 0.9%, would help in separating overlapping line profiles, as would a more intense primary electron beam to increase the signal-to-noise ratio.

The main concern, however, is to obtain the magnitude of the carbon spectral line normalized to some constant response in the spectrum. Often the elastic peak of the primary beam is used for this purpose although in this work the $L_{3M_{4,5}}M_{4,5}$ response from copper (920eV) is more appropriate. In future experiments, we will use a signal integrator to obtain a plot of $N(E)$ vs E rather than the derivative form used to plot the current data. Elemental concentration derived from the $N(E)$ data are far more meaningful than those derived from the $dN(E)/dE$ data.

V CONCLUSIONS AND RECOMMENDATIONS

Preliminary work on lunar soil samples 61501,84 and 64421,11 over the past several months has shown that their particulate morphology is not ideally suited to our investigative technique, as it was initially applied. Results from specimens of soil which had been bonded to a solid copper platen were far more encouraging and with some additional modification we should be able to obtain meaningful carbon analyses from these prepared specimens.

The AES data that has been obtained from sputter-ion cleaned particles to a total of 60 minutes beam time, indicate that carbon is not restricted to the original particle surface but also exists within the body of the material. More definitive data are required to ascertain the validity of this observation, and should carbon be found to exist throughout individual particles, we will then need to determine its radial distribution.

These investigations should be continued on the larger and more coherent particles in the samples on hand. With the replacement of the existing electron gun assembly in the AES with one that has just been delivered, both higher spatial resolution and primary electron beam intensities will again be possible and these qualities should be reflected in the newly generated data. Maximum effort should be concentrated on extracting data from prepared surfaces with the highest spatial resolution possible from the AES.

The problem of extraneous material deposition onto sputter-ion cleaned surfaces during the sputtering process needs to be investigated and geometrical conditions established to eliminate this deposition process.

Finally, when appropriate data are obtained from our specimens, computations

will be required to deconvolute the spectral-line profiles from carbon and other closely similar responses. The resultant data will enable us to obtain a more quantitative evaluation of the carbon distribution profiles in these sample materials.

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The purpose of this work is to investigate radial distribution profiles of elemental carbon in lunar soils consisting of particles in the size range of 50 to 150 μm .

This report is concerned with the initial experiments on specimen preparation and the analysis of prepared specimens by Auger electron spectrometry (AES) and scanning electron microscopy (SEM).

Results from splits of samples 61501,84 and 64421,11, which were mounted various ways in several specimen holders, are given in this report. A low carbon content has been observed in AES spectra from soil particles that had been subjected to sputter-ion cleaning with 960eV argon ions for periods of time up to a total exposure for one hour. This ion charge is sufficient to remove approximately 70 nm of material from the surface. All of the physically adsorbed carbon (as well as water vapor, etc.) would normally be removed in the first few minutes, leaving only carbon in the specimen, and metal support structure, to be detected thereafter.

A number of problem areas have been identified and consideration is given to methods which may be employed to overcome these difficulties.

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I INTRODUCTION

This report describes the progress made in developing a practical method for the determination of both spatial and depth distributions of carbon in lunar fines.

The lunar soils that were collected at the Descartes site during the Apollo 16 mission have been analyzed for their total carbon content⁽¹⁾, and these analyses show the carbon content to lie approximately within the range 60-250 ppm. Comparing these data with carbon data from soils obtained during previous missions, show that the carbon content of most lunar soils is similar⁽²⁾. The origin of carbon found in the lunar regolith is believed to be the solar wind.

The composition of Apollo 16 soils, of which carbon is a very minor constituent, is largely made up of the following materials, SiO_2 (45%), Al_2O_3 (27%), CaO (16%), MgO (6%), and FeO (5%): the numbers in parentheses are averages which were derived from the analyses of all Apollo 16 soils⁽³⁾.

Samples of Apollo 16 soil requested for this investigation were selected on the basis of their overall carbon content and particle size. Four samples were received on April 9, 1976, whose total carbon contents ranged from 65 $\mu\text{g/g}$ to 280 $\mu\text{g/g}$: the sample numbers and sampling locations at the Descartes site are shown in Fig. 1. For optimum utilization of grid openings in the specimen holders we proposed for this research, discrete particles in the size range 50 to 150 μm are necessary. This size range corresponds closely to the 63-125 μm sieved size fraction used in particle size analyses of lunar fines.

In order to equate the carbon content in our samples to either surface or indigenous carbon, a method consisting of argon-ion beam profiling in conjunction

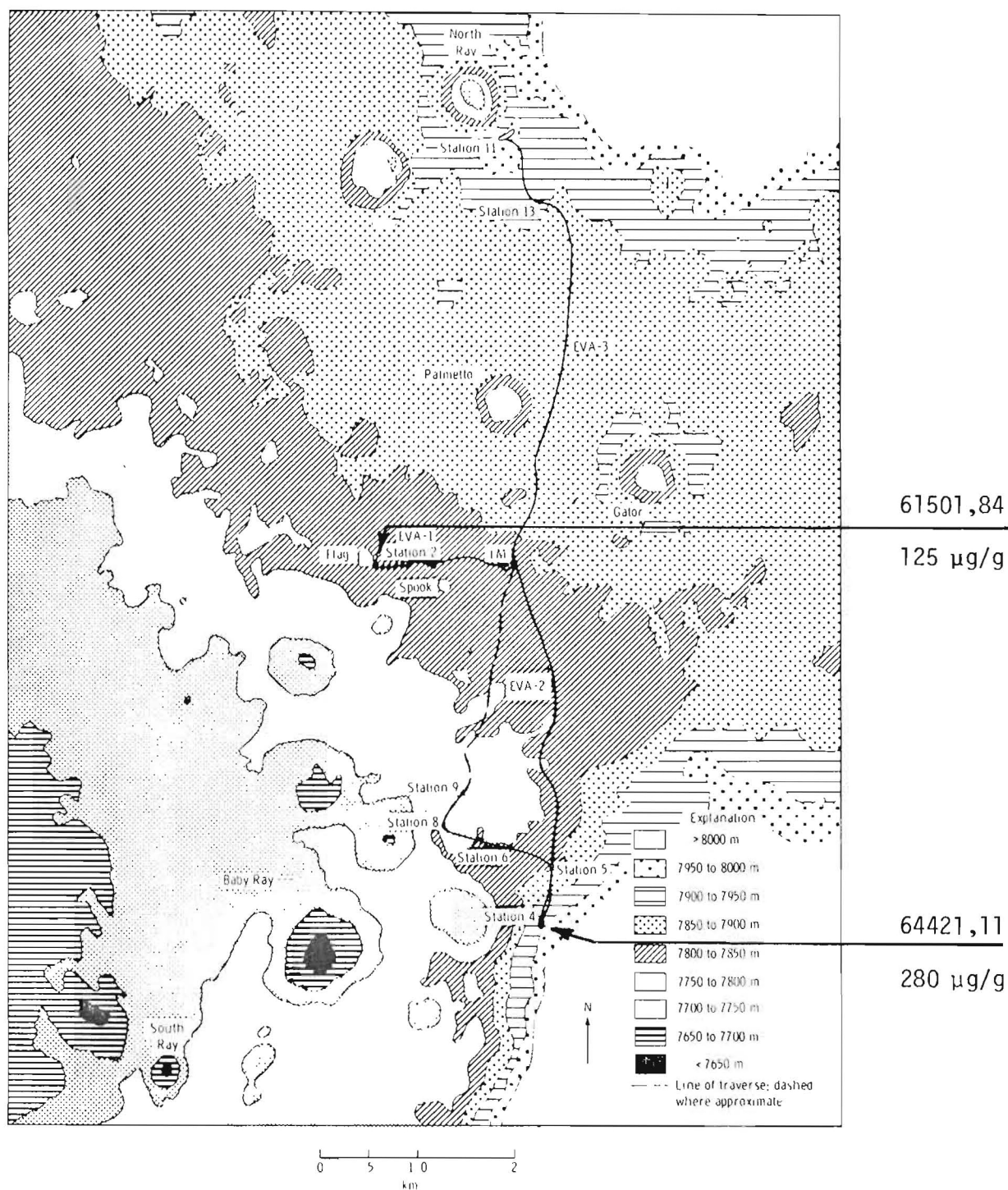


Fig. 1. Hypsographic map of Descartes site showing Lunar Module and sites visited during the Apollo 16 mission (NASA SP-315, p.6-63, 1972). Samples that have been analyzed during this study are listed as well as their reported total carbon content (Ref. 1).

with scanning Auger-electron spectrometric microscopy is being employed⁽⁴⁾,

Auger-electron spectroscopy (AES) is particularly sensitive to the lower atomic number (Z) elements, such as beryllium, boron and carbon. In carrying out AES analyses carbon is almost invariably an obnoxious impurity as well as being the main constituent of surface contamination⁽⁵⁾. Under the environmental conditions used to carry out AES analyses, carbon and other surface contaminants can be readily removed before, as well as during, analysis by bombarding the surface area being analyzed with a beam of ionized argon. However, by so doing, this analytical method can no longer be strictly called non-destructive, since both the sample's mass and surface topography are changed. Also, it must be remembered that material can be removed by, or diffuse from, the primary irradiated zone by reacting with the electron beam⁽⁶⁾. Consequently, it is extremely important to keep the electron dosage as small as is practical during the analysis.

Also, quantitative analysis of a profiled surface must take into consideration changes in the surface topography due to selective removal of material while under ion-beam irradiation. Topographical features are most successfully monitored by scanning electron microscopy.

II EXPERIMENTAL

A. Material

Four samples of Apollo 16 soil, each having a mass of approximately 0.1g, were received on April 8, 1976. The sample numbers were: 61501,84; 64421,11; 65701,68; 67701,9. Up to the time of writing this report only the sample containers holding samples 61501,84 and 64421,11 have been opened. These two samples were observed to be light grey powders. During subsequent handling of some of the particles with "demagnetized" stainless steel tweezers, they appeared to be slightly magnetic.

Scanning electron micrographs taken of very small portions of these powders during the course of this investigation showed the grain size in these two samples to vary from about 3 μm to over 300 μm . Furthermore, most of the particles in the size range of interest (50-150 μm) were observed to be agglutinates of varying sized particles, as shown in Figs. 2 and 3, and not discrete particles. This feature has proved to be particularly troublesome and has resulted in technique changes and some undesirable results. We will return to this question of particle morphology at various places throughout this report.

B. Specimen Preparation.

1. Environmental Chamber. The original intention for preparing samples for AES analysis, as described in our proposal, was to carry out all the specimen preparation in a stainless steel environmental chamber under a slight positive pressure of dry nitrogen. Because of the nature of the sample material, it was found to be unpractical to handle the material via the rubber gloves protruding through the chamber wall.

As a solution to this problem, samples to date have been loaded into



Fig. 2. SEM of sample 64421,11a attached to copper platen with conductive silver paint.

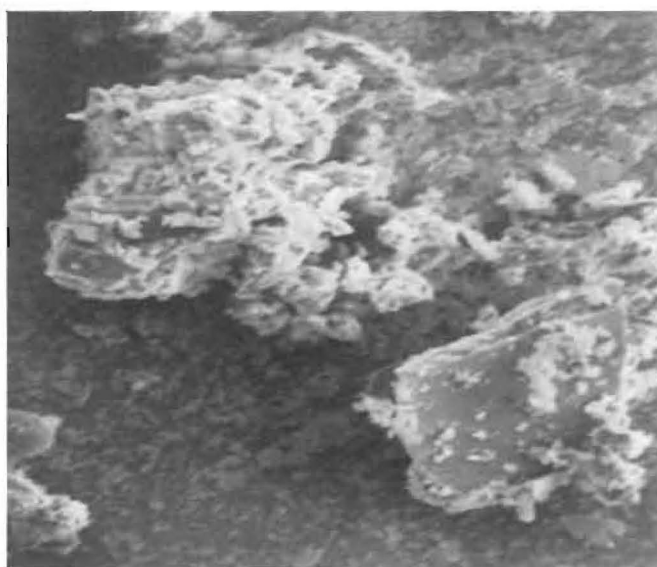


Fig. 3. SEM of another area of mounted specimen used in Fig.17. Note range of particle sizes from several microns to over 300 microns,

holders within the environmental chamber under atmospheric conditions with the front glass cover partly opened and the whole of the preparation area illuminated with moderately intense ultraviolet radiation. This technique has been shown to prevent carbon buildup on clean surfaces⁽⁷⁾, and should prevent all but the very minimum buildup of carbon on our samples before they are subjected to AES analysis - this carbon is customarily removed during the first ion cleaning step.

The transfer of soil to the grids, and the grids to the holder were carried out under a variable magnification stereo microscope. All the specimen handling equipment, including the specimen support screens and holders, were thoroughly cleaned before use in the environmental chamber or for transport of specimens to the spectrometer, etc.

This cleaning process consists of the following steps:

- 1) Vapor degrease components in trichloroethylene.
- 2) Ultrasonically clean in an aqueous solution containing 50 ml of MICRON[®] per liter.
- 3) Wash in distilled water and rinse in a stream of methanol (ACS grade).
- 4) Immerse in a hydrogen peroxide (30 percent) solution containing 10 percent ammonium hydroxide, effervescing at 80°C. Remove after the liquid is spent.
- 5) Rinse in a stream of methanol and dry in a stream of pure nitrogen.
- 6) Transfer items to the environmental chamber.

Items that have been cleaned by this procedure have been found to be free from carbon as a surface contaminant.

2. Specimen Grids and Holders. A specimen holder was designed so as to

make use of the quick charge, plug in, feature of our electron spectrometer. One of the two units is shown in Fig. 4. The base is a commercially manufactured type HC-6 base of a quartz resonator container and mates with a two pin ceramic bodied socket, which is mounted on the specimen manipulator in the AES.

The round specimen holder section holder section is attached to a molybdenum support bracket with a 2-56 stainless steel screw. In turn, the specimen grid is secured against a flange at the bottom of the opening by a copper collar which bears against the molybdenum support bracket. The round section is made from very high purity copper and is heavily gold plated.

A 200 mesh hinged gold grid (see Fig. 5) was selected at the beginning of this project to mount the lunar soil samples. On shaking a small amount of sample 61501,84 onto such a grid, it was quickly discovered that essentially all the soil particles fell through the 90 μm openings. Then, all except one on two particles that remained on the grid broke up and passed through the grid when it was folded and secured in place by the retaining ring.

Some 400 mesh (40 μm openings) copper grids were on hand so an attempt was made to use this type of grid. A few more particles were retained between these grids, but they presented another problem - a greatly reduced free area. Also, it was observed that the captured particles were not securely held in the grid sandwich because of the grid's flexibility. Some results were obtained from soil supported between 400 mesh grids.

Another approach was used in preparing the last sample that we have analyzed. The technique was to replace the rear grid with a solid copper platen (25 μm thick) and to attach soil particles to it with a very thin layer of silver conducting paint. This paint is composed of pure silver particles suspended in



Fig. 4. View looking in the primary beam direction
x4
of a specimen holder used to mount lunar
fines for AES/SEM.

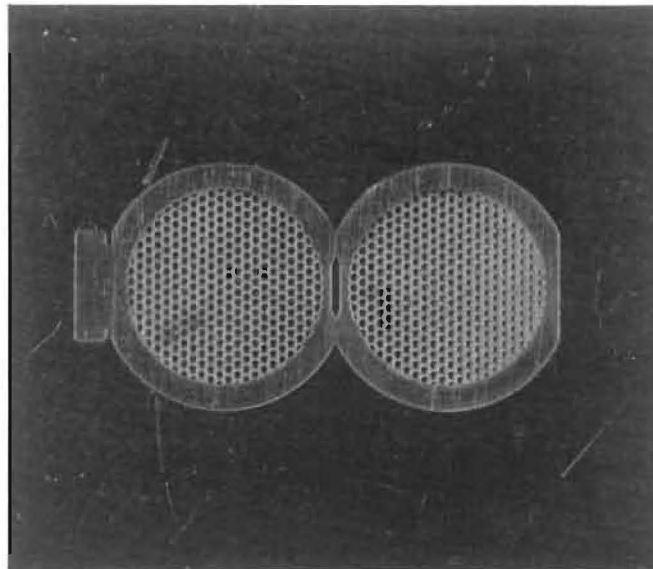


Fig. 5. View of a 200 mesh hinged gold specimen
x11
mount.

ethanol. A 300 mesh hexagonal copper grid (50 μm openings) was used to complete the specimen mount.

C. Analysis

Electron spectrometric analyses were carried out in the scanning Auger electron spectrometer shown in Fig. 6. The system uses a cylindrical mirror analyzer (J) with a 1 percent energy resolution, a 0-5 keV primary electron gun (D) and a 0-1 keV Argon ion gun (L). Three electrostatic lenses in the electron gun focus the beam to about an 8 μm diameter spot in the specimens plane (M). Deflection coils (E) allow the beam to be scanned on the specimen surface in a variety of ways, e.g., raster, line scan, point-to-point. A minimum image magnification of 28 can be obtained in the meter mode. The ion beam can be focused to about a 4mm spot on the specimen, which is rotated about 90° to receive the ion beam.

Auger-electron data were obtained with the spectrometer system operating at a base pressure of $1.2 \times 10^{-7} \text{ N/m}^2$ (9×10^{-10} torr). During the majority of runs, an electron beam energy of 3900eV was used, although experimental runs were made with the beam energy as low as 1200eV. In all instances, the beam current at the specimen was about $2 \times 10^{-8} \text{ A}$.

In order to reduce charging and also to prevent radiation induced changes to the specimens, the primary beam was always scanning the specimen. AES data were usually collected with the electron beam scanning the desired area of the specimens surface at a rate of one frame per 8 seconds. At a magnification setting of 1.52 (x306), a rectangular specimen area 400 μm long by 300 μm wide was illuminated. This area encloses about 9 openings in a 300 mesh grid.

Argon ion cleaning and profiling was carried out at an argon pressure of $7.7 \times 10^{-3} \text{ N/m}^2$ (5.8×10^{-5} torr). The ion gun was operated in the focused condition

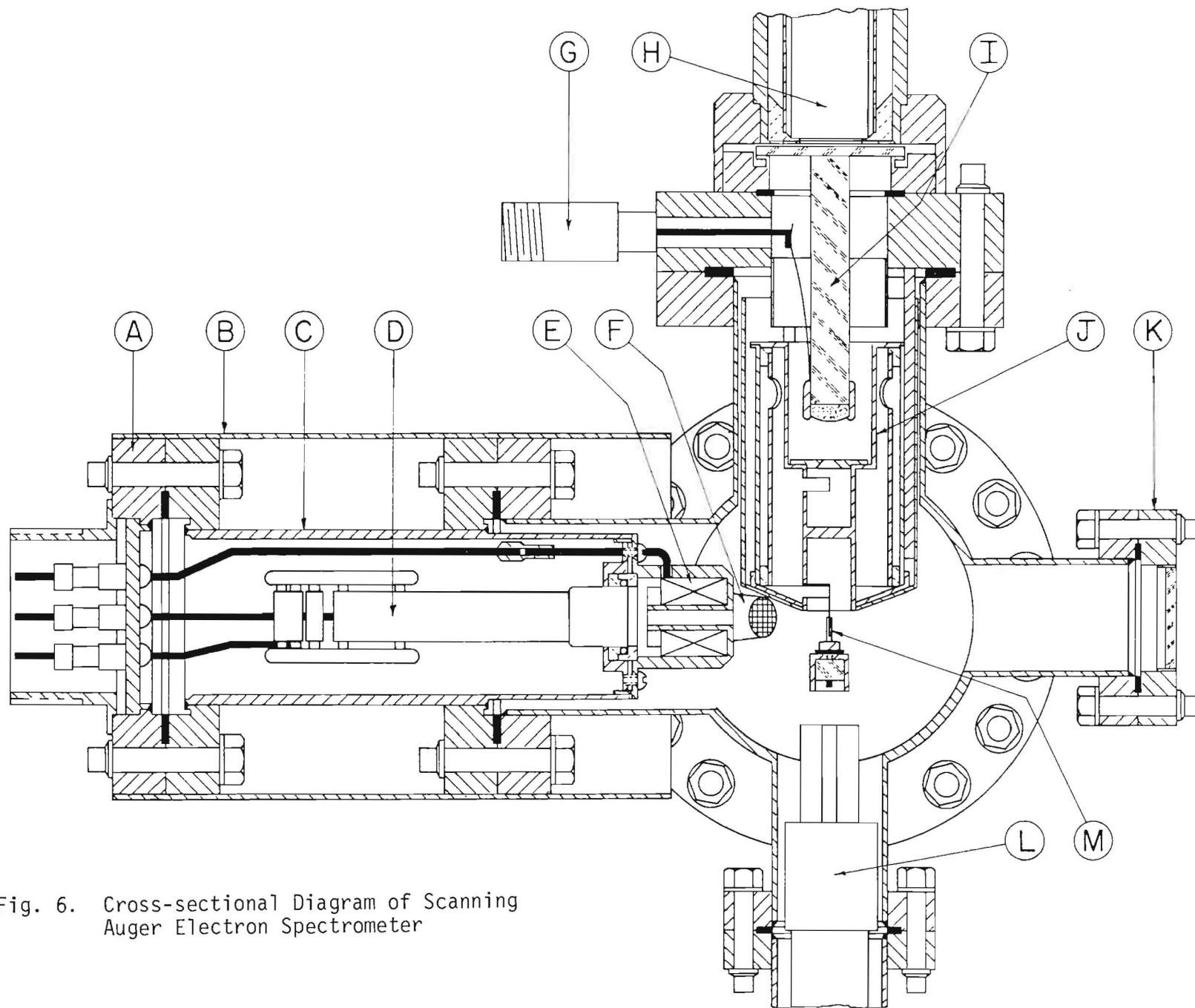


Fig. 6. Cross-sectional Diagram of Scanning Auger Electron Spectrometer

at 960eV and 8×10^{-6} A.

Each ion bombardment was for a period of 15 minutes, which corresponds to the removal of approximately 45nm (rate of 3nm/min). This sputtering rate was determined from earlier work on quartz surfaces. Also, in the case of quartz, carbon and water surface contaminants were completely removed during the first 4 minutes of ion bombardment.

Low resolution absorbed current images were recorded of the areas used to obtain AES data. These images were used to reidentify the analyzed regions of each sample when the samples were examined in a regular SEM. The complete holder was mounted in the SEM so as to avoid disrupting the particles in the specimen from their original positions.

III RESULTS

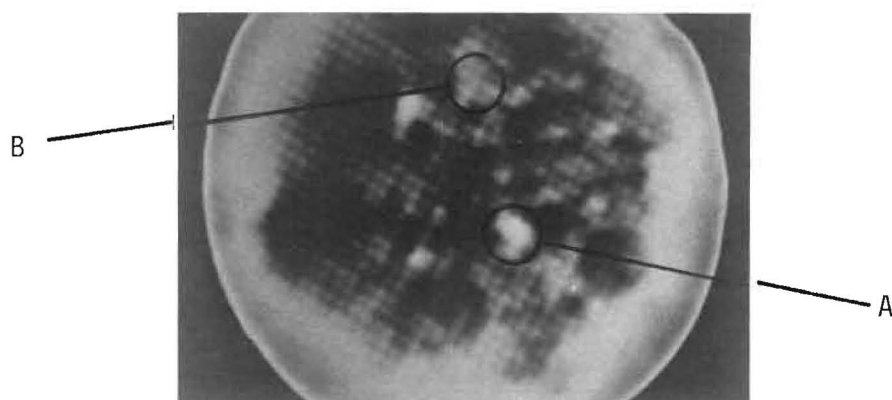
A. Sample 61501,84

Three specimens have been prepared from this sample. From the first split, 84a, two specimens were prepared, the first with the soil particles between 200 mesh gold grids, and the second with the soil particles between 400 mesh copper grids. The second split, 84b, was used between two 300 mesh hexagonal copper grids.

Although the specimen using 200 mesh grids was subjected to AES examination, no useful data were obtained. This situation was due to the non retention of the soil particles by the grids.

When a switch to 400 mesh grids was made, a sufficient number of soil particles were retained in the grid sandwich to show up in the electron images, see Fig. 7, which were recorded in the AES. Several of the larger particles were selected for AES analysis.

Before the lunar soil was placed between the two 400 mesh grids used to prepare specimen 61501,84a, the grids were mounted in the specimen holder and analyzed in the AES. An initially strong carbon peak was essentially removed from the spectrum by sputter-ion cleaning for 15 minutes, as is shown in Fig. 8. This procedure was also carried out in all successive runs to obtain a data base from the specimen supports. With soil particles in position a prominent carbon peak was again a prominent component of the AES spectrum. However, after sputter-ion cleaning for 15 minutes, the carbon peak was substantially reduced and many other spectral lines appeared, as shown in Fig. 9. The elemental contributions from the soil particles are calcium, carbon, iron,



x28

Fig. 7. Image of sample 61501,84a in the AES before analysis. Areas marked by A and B were selected for AES.

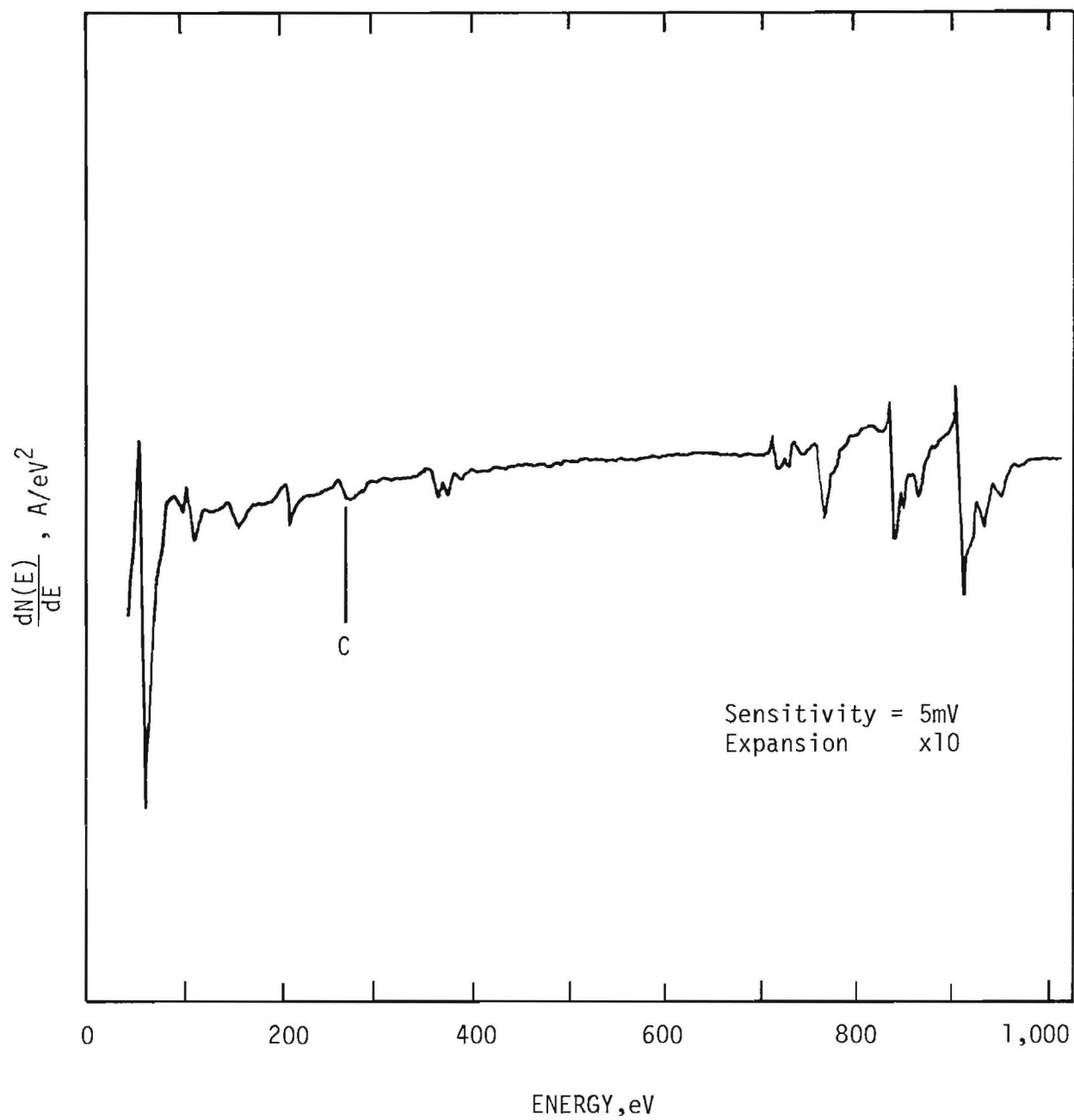


Fig. 8. AES from a 400 mesh copper grid in gold plated copper holder #2. Exposed surface was ion cleaned for 15 minutes.

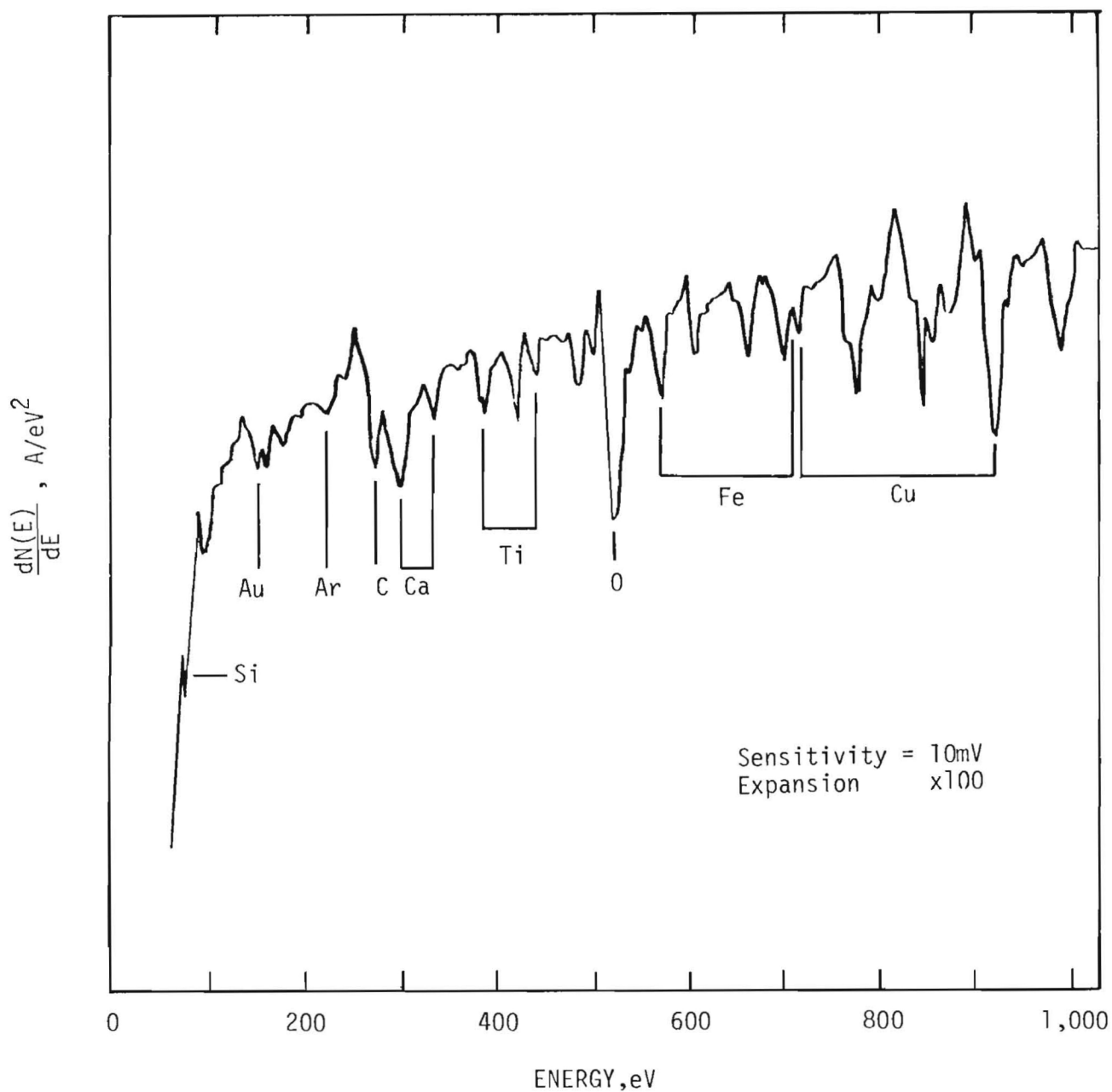


Fig. 9. Sample 61501,84a contained between two 400 mesh copper grids. AES recorded after 15 minutes of sputter-ion cleaning.

oxygen, silicon and titanium. The copper is from the support grids and the gold from the holder - sputtered onto the sample area.

After several more 15 minute ion bombardment periods, the spectrum in Fig. 10 was obtained. At this point of time, most of the elemental contributions from the soil had disappeared, with the exception of carbon, iron and oxygen.

Observation of the exposed specimen surface by SEM after a total of 60 minutes of ion bombardment showed the remaining particles to be generally smaller than the grid holes and scattered around the central region of the grid - see Figs. 11 and 12. None of the samples were metallized before SEM examination, so a certain amount of charge buildup was experienced. This effect is seen as horizontal streaking in the electron micrographs. Although the charging effect detracts from the quality of the image, it is easy to see under moderate magnification conditions (see Fig. 13) that the larger particles are agglutinates and not solid chunks. From the observed change in the AES data between 15 and 45 minutes, it is reasonable certain that the ion bombardment contributed to a breakdown and scattering (with considerable loss of material) of particles over the outer grid surface.

The AES data we obtained from the 84b split were essentially the same as those data given for the 84a split and will not be repeated herein.

B. Sample 64421,11a

Only one specimen has been prepared from this soil sample to date. The method of specimen preparation using a solid platen and silver paint appears to have considerable possibilities in this type of investigation. As Fig. 14 shows, a few large particles were securely anchored into place, but their

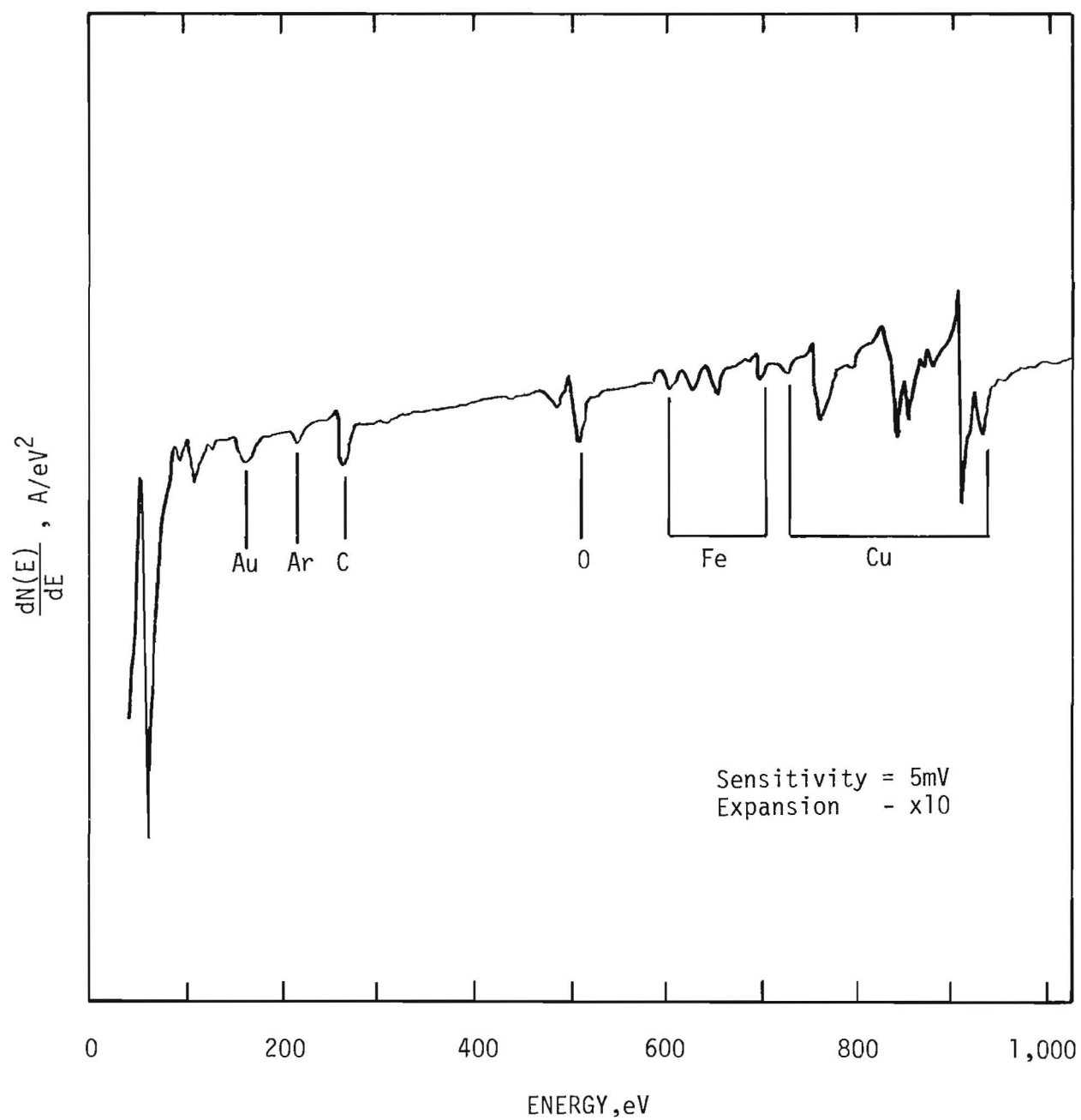
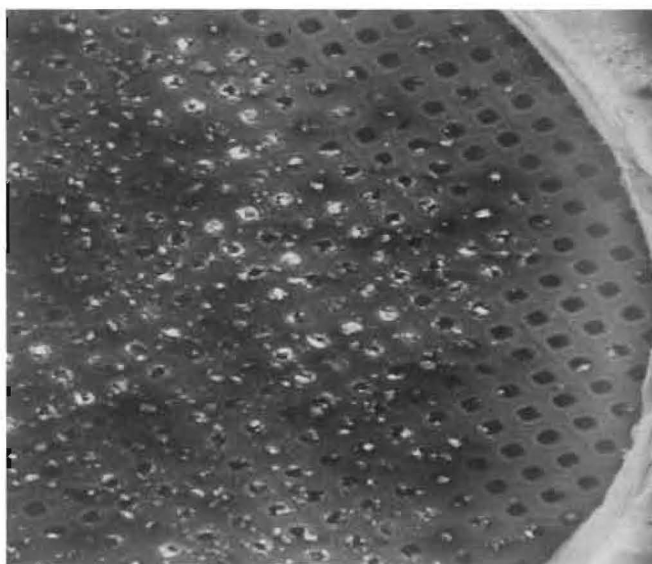
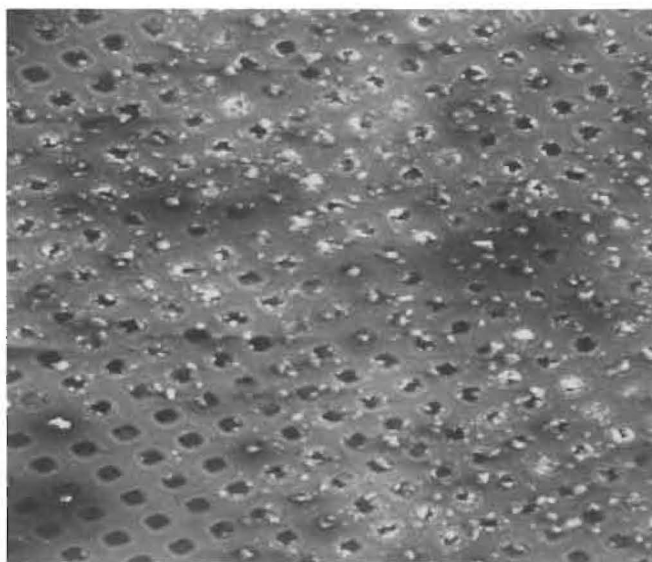


Fig. 10. AES from area B (see Fig. 7) of sample 61501,84a after 45 minutes of sputter-ion cleaning.



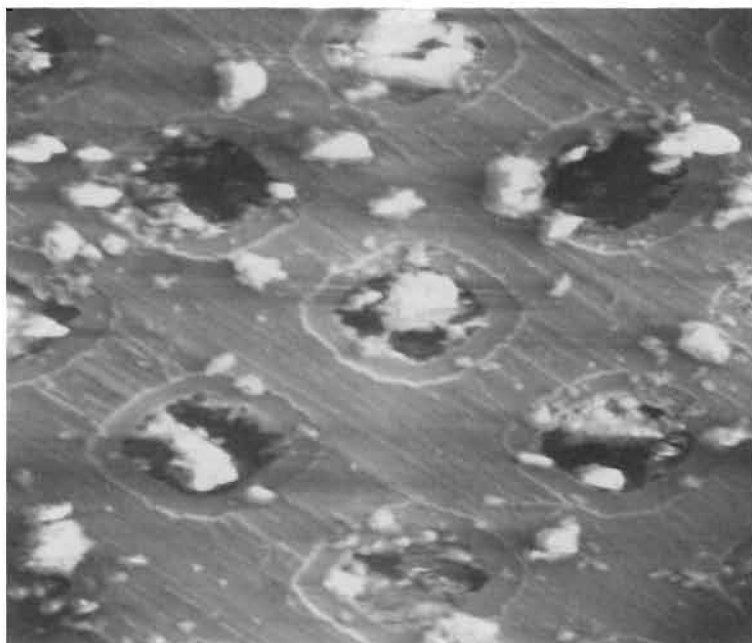
x60

Fig. 11. Section of 400 mesh grid containing particles of sample 61501,84a after AES analysis. Area A in Fig. 7 is located near top center in this view.



x60

Fig. 12. SEM from near center of same grid as shown in Fig. 11. Area B in Fig. 7 is located near left center of this image.



x350

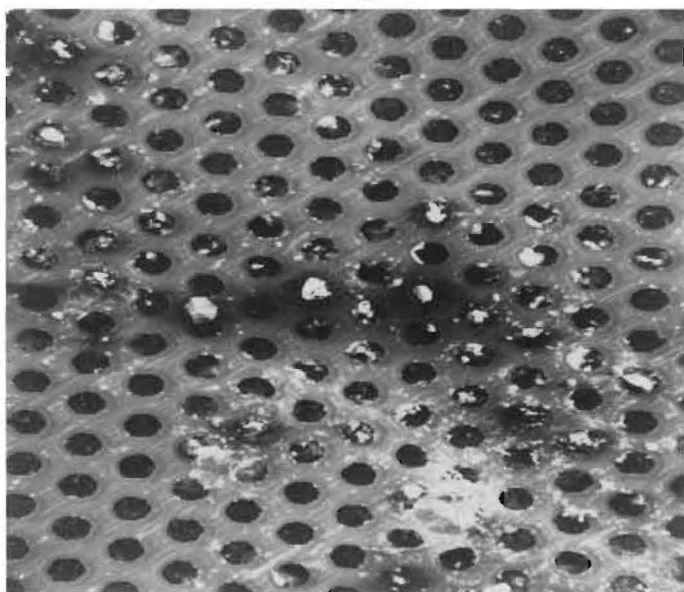
Fig. 13. Higher magnification SEM of part of the image shown in Fig. 12. Note the wide variation in particle size.

exposed areas were rather minimal. The use of grids with larger openings, e.g., 200 mesh or even 100 mesh, is indicated. However, if too large a grid structure is used, one runs the risk of electric charge buildup on the particle surface.

The degeneration of the ion bombarded particle surface into much smaller particulate matter is again evident in Fig. 14.

The AES shown in Fig. 15 was recorded from an as-prepared specimen of sample 64421,11a, with an ion cleaned 300 mesh copper support grid. Although the carbon peak is substantial, there was not sufficient carbon on the irradiated specimen surface to completely absorb all the Auger electrons from both the particulate matter and the front surface copper grid. Note that the response from silver is weak. With suitable screening, it should be possible to exclude the contribution of silver, and any associated carbon in the silver paint, from the primary spectrum.

After a total sputter-ion cleaning period of one hour, the copper response is dominant, see Fig. 16, but the carbon spectral line is still present, although it is reduced in height by a factor of 6 from the initial scan (Fig. 15). If future experiments can positively associate this carbon with particles, then we can begin to relate these carbon data to distribution profiles within the particle.



x78

Fig. 14. SEM from near center of sample 64421,11a. Soil particles were attached to solid copper platen with silver conducting paint and covered with a 300 mesh copper grid. Sample was sputter-ion cleaned for 60 minutes. AES data were recorded from the protruding particle at lower left center.

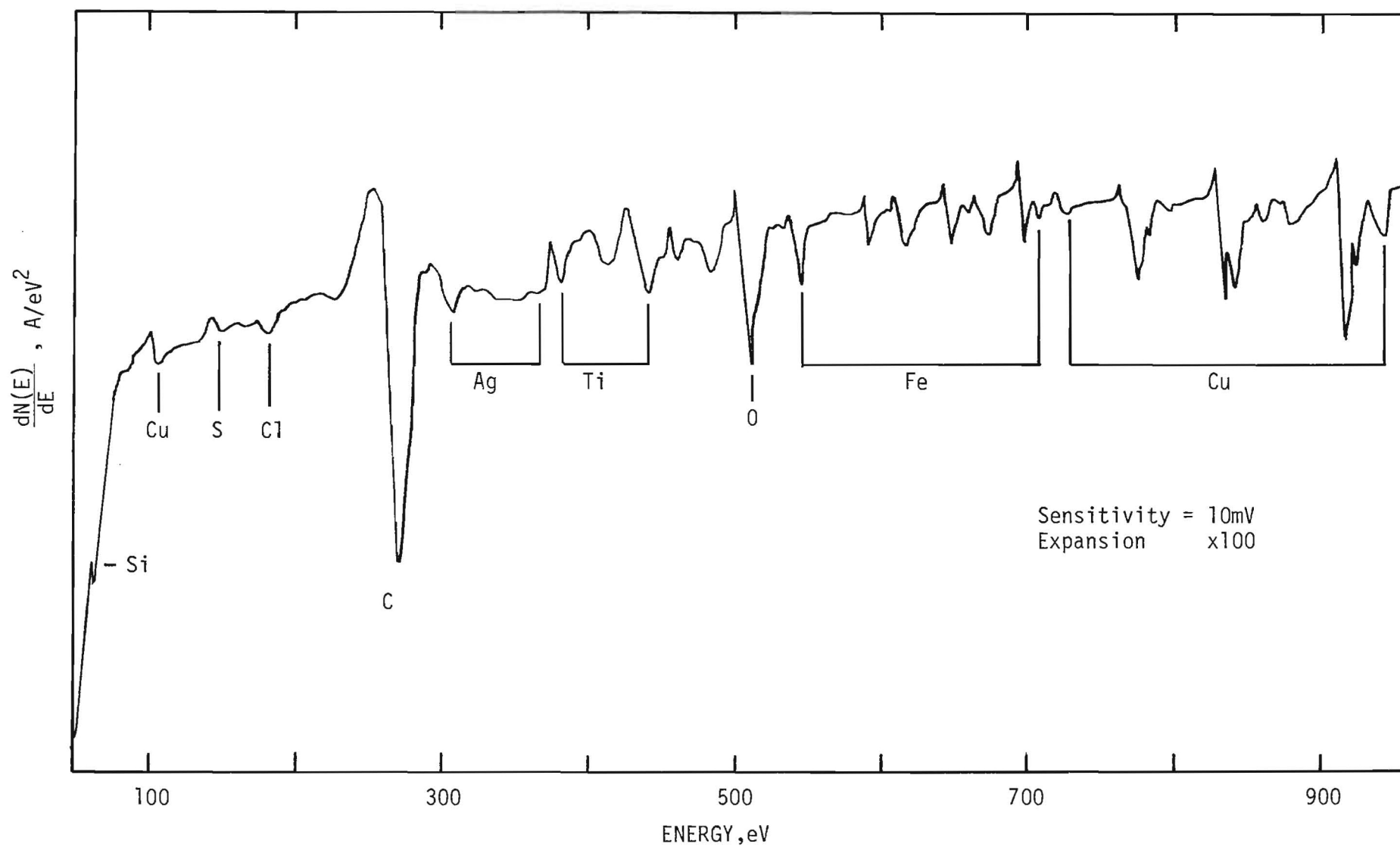


Fig. 15. Sample 64421,11a as shown in Fig. 14. This plot was recorded before the sample was subjected to any sputter-ion cleaning.

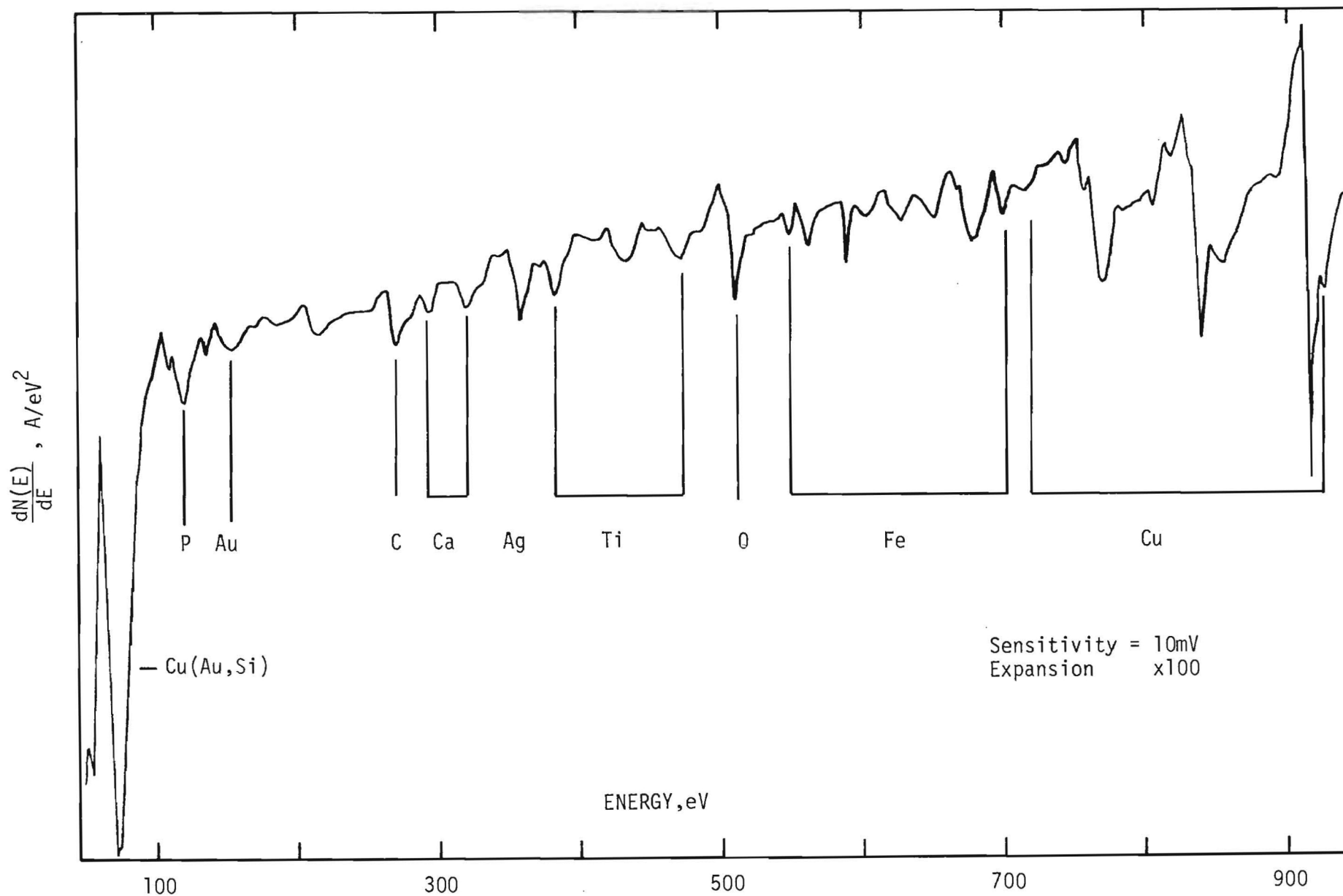


Fig. 16. AES from sample 64421,11a after the fourth successive 15 minute sputter-ion clean.

IV DISCUSSION

From the time of the first viewing of these lunar soil samplings, it was obvious that an innovative method would have to be devised to handle the specimen preparation. The initial concept of sandwiching discrete particles between microscope support grids with appropriately sized grid openings has previously been found to work well in both AES and SEM examinations.

In the present application of this technique only a very few physically homogeneous particles of suitable size were encountered in the samplings. The larger particles in the mounted specimens that have been mounted to date were mainly agglutinates which readily broke down into much smaller particles during mounting and/or during sputter-ion cleaning.

It should be possible to obtain a sufficient number of particles of the type shown in Fig. 3 to make up a specimen by sieving the soil samples through a grid and then selectively remove a suitable number of particles from the retained screenings. The present results indicate that it will still be necessary to adhere these particles to a platen with silver paint. There is still the possibility that these particles will break up during ion bombardment, and should this occur, it will have to be concluded that it will not be feasible to analyze these samples by depth profiling in the AES. Should this situation develop, then either a different type of sample will be necessary, or else the whole procedure dropped as being unsuitable for investigating this particular type of material.

The presented AES data show that material (gold in the present case) which has been removed by ion bombardment can easily deposit on the cleaned surface.

Naturally, the deposited material will exclude Auger-electron data from the derived spectra. Preventing this deposition process from occurring is difficult to accomplish, especially when the target area consists of both metals and insulators.

Sometimes it is possible to change the redeposition rate of the sputtered materials by changing the incident angle of the ion beam. However, if this angle is greatly increased from the surface normal, anisotropy is more likely to occur in the sputtering process and with our type of specimen shadowing may be an important factor. Neither of these effects are as important as the prevention of the material deposition during sputter-ion cleaning. No quick solution in this problem area is foreseen.

Another difficulty in quantifying the carbon response in the current spectral data is the partial overlapping of the carbon and calcium responses in the energy range between 260 and 300eV. This feature is noticeable in Figs. 9 and 16 with the carbon line (272eV) and the calcium doublet (291 and 294eV). A higher resolution spectrometer than the one used in this work, which has an energy resolution of 0.9%, would help in separating overlapping line profiles, as would a more intense primary electron beam to increase the signal-to-noise ratio.

The main concern, however, is to obtain the magnitude of the carbon spectral line normalized to some constant response in the spectrum. Often the elastic peak of the primary beam is used for this purpose although in this work the $L_{3M_{4,5}}M_{4,5}$ response from copper (920eV) is more appropriate. In future experiments, we will use a signal integrator to obtain a plot of $N(E)$ vs E rather than the derivative form used to plot the current data. Elemental concentration derived from the $N(E)$ data are far more meaningful than those derived from the $dN(E)/dE$ data.

V CONCLUSIONS AND RECOMMENDATIONS

Preliminary work on lunar soil samples 61501,84 and 64421,11 over the past several months has shown that their particulate morphology is not ideally suited to our investigative technique, as it was initially applied. Results from specimens of soil which had been bonded to a solid copper platen were far more encouraging and with some additional modification we should be able to obtain meaningful carbon analyses from these prepared specimens.

The AES data that has been obtained from sputter-ion cleaned particles to a total of 60 minutes beam time, indicate that carbon is not restricted to the original particle surface but also exists within the body of the material. More definitive data are required to ascertain the validity of this observation, and should carbon be found to exist throughout individual particles, we will then need to determine its radial distribution.

These investigations should be continued on the larger and more coherent particles in the samples on hand. With the replacement of the existing electron gun assembly in the AES with one that has just been delivered, both higher spatial resolution and primary electron beam intensities will again be possible and these qualities should be reflected in the newly generated data. Maximum effort should be concentrated on extracting data from prepared surfaces with the highest spatial resolution possible from the AES.

The problem of extraneous material deposition onto sputter-ion cleaned surfaces during the sputtering process needs to be investigated and geometrical conditions established to eliminate this deposition process.

Finally, when appropriate data are obtained from our specimens, computations

will be required to deconvolute the spectral-line profiles from carbon and other closely similar responses. The resultant data will enable us to obtain a more quantitative evaluation of the carbon distribution profiles in these sample materials.

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